

# EXPERIMENTAL ORGANIC CHEMISTRY



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# EXPERIMENTAL ORGANIC CHEMISTRY

*by*

*Augustus P. West, Ph.D.*

*Professor of Chemistry, University of the Philippines*

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## PREFACE

IN several respects this book is somewhat different from similar ones which are in general use at the present time. It is a combination of textbook and laboratory manual in which the theoretical discussions and the laboratory experiments are blended together. This arrangement encourages the student to consult the text while he is doing the experiments in the laboratory, with the result that he is more likely to perceive clearly the relation between the theory and the practice.

Only the more important compounds are discussed, and thus the student is not bewildered with a mass of information relating to a large number of compounds of minor importance. Again, experiments which are dangerous or very difficult for a beginner have been purposely omitted.

The application of general reactions and the general relations between the different groups of compounds have received special attention; in fact, at frequent intervals review tables are given, showing the relation between the principal members of various groups of compounds. These review tables are very helpful in enabling the student to review at a glance the chemistry of a number of groups of compounds.

Special emphasis has been laid upon the exact preparation of organic compounds, as this constitutes the most important feature of a course in organic chemistry. In accordance with this view the directions for performing the experiments have been written in a most precise and accurate manner and will be found unusually free from ambiguous statements; in fact, the student is usually told exactly what to do and how to do it. This method has given excellent results in the University of the Philippines, where it has been necessary to handle laboratory sections of more than one hundred students. It trains a student to follow directions and to rely upon himself rather than an instructor, it enables a teacher to handle large laboratory classes in a satisfactory manner, with the result that accidents and explosions seldom, if ever, occur.

Unlike many laboratory manuals, this book gives the equations to explain the experiments, as it is considered desirable to give the student ample opportunity to understand thoroughly his laboratory

work. Questions relating to the experiments and other questions which are supposed to give a certain amount of mental training are placed at the end of the chapters.

This book may be used as a combination textbook and laboratory manual, in which case material that has been omitted, such as certain groups of compounds and experiments, may be presented in the lectures. Since the text itself is rather abbreviated, some teachers, in giving a more extended course, may perhaps prefer to use the book simply as a laboratory manual.

The author wishes to express his sincere thanks to Mr. J. I. Del Rosario, Miss P. P. Herrera, and Miss Zoila Montes of the University of the Philippines, who have assisted him in reading the proof.

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## INTRODUCTION

PRIOR to the nineteenth century chemistry was divided into two branches, inorganic and organic. Compounds which could be obtained from living matter such as animal and vegetable substances were called *organic compounds*, and those obtained from inert or mineral matter were known as *inorganic compounds*. For many years it had seemed impossible to prepare organic compounds by artificial methods, and consequently it was believed that organic substances were formed only in a living organism under the influence of a peculiar "vital force." Wöhler in 1828 prepared the organic compound urea,  $\text{CO}(\text{NH}_2)_2$ , which is a typical secretion of the animal organism, from the inorganic substance ammonium cyanate,  $\text{NH}_4\text{OCN}$ . Some years later other organic substances which occur naturally in plants and animals were prepared artificially, and gradually it came to be generally recognized that the influence of a living organism is not necessary for the production of organic compounds.

In recent years the development of organic chemistry has made enormous strides. Theories have been developed which have enabled us to discover a large number of new compounds, many of which are of considerable practical importance. Thus there has been opened up gradually the great field of synthetic organic chemistry; that is, the laboratory preparation of compounds, many of which occur naturally in plants and animals. Since all these compounds contain carbon, *organic chemistry is the chemistry of carbon compounds*.

Although there is no essential difference between organic and inorganic substances, the carbon compounds are still, for various reasons, considered as a separate branch of chemistry. The carbon compounds differ somewhat from the inorganic compounds in their general properties and chemical behavior, and since the number of these compounds is exceedingly large, it is convenient to treat them separately.

The two fields of chemistry, inorganic and organic, overlap to some extent, since certain classes of compounds which contain carbon, such as the cyanogen compounds, may be considered from the standpoint of either branch of chemistry. A more exact name for organic chemistry would be, perhaps, the chemistry of the hydrocarbons and their derivatives, since a large number of organic compounds may be regarded as derived from certain fundamental substances called *hydrocarbons*.



## ALIPHATIC COMPOUNDS



# EXPERIMENTAL ORGANIC CHEMISTRY

## CHAPTER ONE

### PURIFICATION OF COMPOUNDS, SOLVENTS, AND DETERMINATION OF FORMULAS

A LARGE proportion of the compounds of carbon are prepared in the laboratory, from certain substances which occur naturally. The laboratory methods which are used to prepare these compounds have been worked out by careful experimentation.

**Sources of carbon compounds.** In certain parts of the world an oil called *petroleum* is obtained either from natural springs or from wells. This oil is composed chiefly of the paraffin hydrocarbons. By means of the proper methods of purification and preparation, a number of organic compounds can be obtained which are derivatives of these hydrocarbons. When coal is heated for the purpose of manufacturing illuminating gas, a mixture of substances, which is called *coal tar*, is obtained as a by-product. Coal tar yields a number of important carbon compounds. A number of trees and plants also contain organic compounds which are of great value for their medicinal properties. They, therefore, also form a natural source of carbon compounds.

**Purification of compounds.** In order to study the chemical behavior of compounds we must first obtain them in pure condition. The usual methods of purification are the following :

Purification of compounds	Liquids	{ Distillation	{ Determine boiling point for purity
	Solids	{ Crystallization and sublimation	{ Determine melting point for purity

If the substance is a liquid it is purified by distillation, but in the case of a mixture of liquid compounds it is often very difficult to obtain these compounds in pure condition. However, we can subject the mixture to *fractional* distillation and obtain portions which have an amount of a particular ingredient greater than the original mixture. The laboratory method of manipulation is illustrated in the following experiment:

### EXPERIMENT 1

#### Fractional distillation of a mixture of ethyl alcohol and water

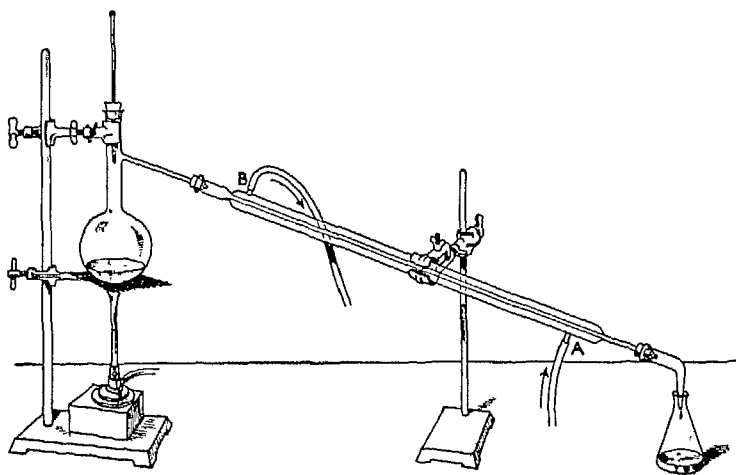


Figure 1

*Materials* { 50 cc. ethyl alcohol (95 per cent)  
100 cc. water

**NOTE.** Before performing any of the experiments the student should read the general laboratory directions which are given in the Appendix.

**Procedure.** Connect a 300 cc. distilling flask to a Liebig condenser, as shown in the figure and place a wire gauze under the distilling flask. The side tube of the distillation flask and the inner tube of the condenser should project a short distance so that the distillate will not touch the stoppers and become contaminated.

Prepare in a beaker a mixture consisting of 50 cc. of ethyl alcohol (95 per cent) and 100 cc. of water. *Will the mixture ignite when a flame is applied to it?* The mixture is poured through a funnel into the 300 cc. distilling flask. A thermometer is passed through a cork stopper and placed in the neck of the flask at such a height that the mercury bulb stands at the same level as the side exit tube of the flask. A moderately slow stream of tap water is allowed to enter the condenser at *A* and flow out at *B*.

Select four clean, dry flasks of about 100 cc. capacity to serve as receivers for the distillate, which is the liquid that distills through the condenser. Number the flasks 1, 2, 3, and 4. The mixture is now distilled and the distillate collected in fractions in the following manner: Flask No. 1 is placed at the exit end of the condenser. The mixture is now heated by a moderate flame which allows it to distil gradually. When the temperature indicated by the thermometer begins to rise above  $85^{\circ}$ , the distillation is continued but the receiving flask No. 1 is removed and replaced by flask No. 2. When the temperature begins to rise above  $89^{\circ}$ , flask No. 2 is removed and replaced by flask No. 3, and as the temperature rises above  $96^{\circ}$  the distillation is discontinued. The liquid remaining in the distilling flask is now poured into flask No. 4 and allowed to cool. The distillate obtained from the original mixture of alcohol and water is thus separated into four fractions:

- I. Room temperature to  $85^{\circ}$  inclusive.
- II. Above  $85^{\circ}$  to  $89^{\circ}$  inclusive.
- III. Above  $89^{\circ}$  to  $96^{\circ}$  inclusive.
- IV. Above  $96^{\circ}$ .

Measure each fraction and tabulate the results as follows:

	FRACTION	I	II	III	IV
	Temperature	Room Temperature to $85^{\circ}$	Above $85^{\circ}$ to $89^{\circ}$	Above $89^{\circ}$ to $96^{\circ}$	Above $96^{\circ}$
First distillation . . .	Volume				
Second distillation . .	Volume				

The constituents of the original mixture may be further separated by a second fractional distillation. This is carried out in the following manner: The first fraction is placed in a clean distilling flask which is connected to a condenser. Distil until the thermometer indicates a temperature of  $85^{\circ}$ . When the temperature begins to rise above  $85^{\circ}$ , temporarily discontinue the distillation, pour the second fraction into the flask, and continue the distillation without changing the receiving flask. A small amount will distil over before the temperature reaches  $85^{\circ}$ ; when this temperature is obtained stop distilling, and add fraction III and proceed as before. Fraction IV is treated in the same manner, except that when the thermometer begins to rise above  $85^{\circ}$  the flask No. 1 is removed and flask No. 2 is put in its place. At  $89^{\circ}$  the receiver No. 2 is removed and flask No. 3 put in its place. At  $96^{\circ}$  the distillation is discontinued and the residue (fraction IV) remaining in the flask is cooled. The four fractions obtained in the second distillation are measured and the results recorded in a table as represented above. By continued fractional distillation the two end fractions (in this case Nos. I and IV) will increase in volume, while the intermediate fractions will diminish. *Having twice fractioned the mixture of ethyl alcohol and water, ascertain if fraction No. 1 is now sufficiently rich in alcohol to ignite when a lighted match is applied to it.*

Ethyl alcohol boils at  $78^{\circ}$  and water at  $100^{\circ}$ . A mixture consisting of 2 volumes of water and 1 volume of alcohol will begin to boil at about  $78^{\circ}$ , but only a very small amount of the distillate passes over at that temperature; gradually, as the distillation proceeds, the temperature indicated by the thermometer becomes higher and higher until at last  $100^{\circ}$  is reached and all distils over. The distillates obtained at different temperatures differ from each other in composition. Those obtained at the lower temperatures have a larger amount of alcohol than those obtained at the higher temperatures.

**Boiling point.** In determining the purity of compounds which are liquids, the most important physical property utilized is the boiling temperature, or boiling point. The temperature indicated by the thermometer when the liquid is distilling is called



the *boiling point*. In the case of pure compounds the boiling point does not rise during the distillation, but remains constant. For accurate observations the boiling point must be corrected in accordance with the barometric pressure observed at the time of the experiment, since the boiling point varies with the barometric pressure. A correction should also be made for the part of the thermometer which is not inclosed by the flask. Tables for making the necessary corrections may be found in larger laboratory manuals.

The purification of compounds which are solids is effected by crystallizing them.

## EXPERIMENT 2

### Crystallization of urea

*Procedure.* Place about 10 grams of urea in an evaporating dish and add a sufficient amount of hot water to dissolve it. Evaporate the solution on a water bath until a slight residue of the solid is deposited on the side of the dish. Allow the solution to cool and crystallize. Filter, and wash with a few cubic centimeters of water. Then place several thicknesses of filter paper on a watch glass, and on this lay the filter paper containing the urea. The watch glass is used to prevent the moist filter paper from coming in contact with the desk, which may not be thoroughly clean. Place the watch glass containing the urea in your desk and allow it to remain some hours until thoroughly dry, after which determine the melting point.

Another method which is used for purifying solids is called *sublimation*. This procedure will be described later, in the directions given for the preparation of certain compounds

## EXPERIMENT 3

### Determination of the melting point

*Procedure.* A number of melting-point tubes should be prepared in the following manner: A piece of soft glass tubing about 10 cm. in length and 7 mm. in diameter is cleaned by washing it with a warm chromic acid wash solution, after which it is washed with water, and dried by washing with a little alcohol and ether and drawing air through

it by means of a vacuum pump until thoroughly dry. The clean, dry tube is held in a flame and rotated somewhat until the glass softens.

The tube is then drawn out quickly so as to form a long capillary tube. The capillary tube is now broken into lengths of about 4 cm. Each of these small tubes is now sealed at one end. The tubes are placed in a clean bottle, which is stoppered and set aside until ready to be used.

Some finely powdered and crystallized urea is now placed on a watch glass, and the open end of a melting-point tube pushed into the powdered urea until a small amount has entered the tube. The open end of the tube is then turned upward, and by tapping the closed end on the table the powder is shaken down into the tube. When the tube has been filled to a length of about 4 mm., attach it to a thermometer by means of a short piece of rubber tubing. The tube containing the urea is so adjusted that the urea is level with the mercury bulb of the thermometer. The thermometer is now supported from a clamp attached to the upper part of

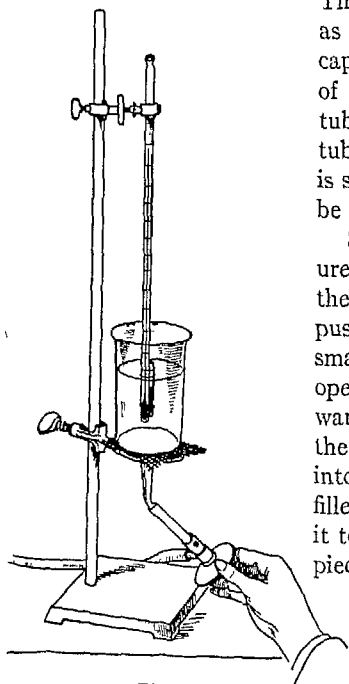


Figure 2

an iron stand, and a 100 cc. beaker containing about 40 cc. of pure sulfuric acid is placed under the thermometer on a wire gauze supported by a ring stand and adjusted so that the bulb of the thermometer is immersed in the sulfuric acid. Take care that the rubber tubing does not touch the sulfuric acid, as the rubber will cause the acid to turn dark so that you cannot observe the melting-point tube. A diagram of the apparatus is shown in Figure 2.

The sulfuric acid is now heated gradually with a small flame which is rotated about the bottom of the beaker. Have your eyes level with the beaker, and looking through the sulfuric acid observe the melting-point tube carefully. The instant the urea melts, observe the thermometer reading which indicates the melting point. If the sub-

stance is pure, it usually melts suddenly. When the sulfuric acid has cooled, it should be poured into a bottle, stoppered, and set aside for other melting-point determinations.

A pure compound gives a sharp, constant melting point; and if the substance does not melt completely at a certain temperature, it is probably an impure compound. To obtain the true melting point, corrections should be made as in the case of the boiling point.

**Organic solvents.** While water is the principal solvent employed for inorganic compounds, a large number of organic substances are insoluble in water and consequently other solvents must be employed to get them in solution. Some of the principal solvents used for organic compounds are the following: ethyl alcohol, methyl alcohol, ether, benzene, carbon bisulfide, petroleum ether, and chloroform. These solvents all boil at temperatures below  $100^{\circ}$  and are inflammable; hence great care must be exercised in using them.

#### EXPERIMENT 4

##### Organic solvents

*Procedure.* Pour about 3 cc. of aniline,  $C_6H_5NH_2$  into each of three test tubes. Add about 10 cc. of water to the first test tube and shake. Does the aniline dissolve? Add about 10 cc. of alcohol to the second test tube and 10 cc. of ether to the third, and shake. Does the aniline dissolve in the alcohol and ether?

Perform a similar experiment, using about 0.5 gram of camphor,  $C_{10}H_{16}O$ , in place of the aniline, and note the results. Aniline and camphor are organic compounds which will be considered later in the course of our study of carbon compounds.

**Composition of organic compounds.** When an organic compound has been prepared in the crude condition and purified by distillation, crystallization, or sublimation, the next step in the investigation of the compound is to analyze it and determine its exact composition. Some organic compounds contain only carbon and hydrogen. However, a large number of organic

compounds consist of these two elements united to one or more other elements such as oxygen, chlorine, or nitrogen.

**Qualitative analysis.** Qualitative tests should be made to detect the presence of the various elements which the compound may contain. In the following experiments are given the qualitative tests for a few of the more common elements present in organic compounds.

#### EXPERIMENT 5

##### Test for carbon in organic compounds

*Procedure.* Heat about 1 gram of cane sugar on the end of a porcelain spatula; notice that the sugar becomes dark in color, chars, and gases are evolved which burn, indicating the presence of organic matter.

#### EXPERIMENT 6

##### Test for carbon and hydrogen in organic compounds

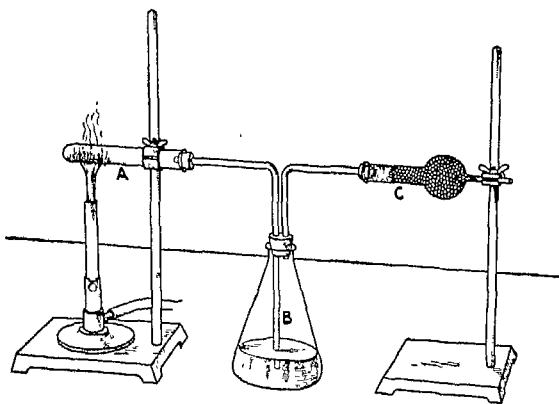
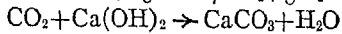
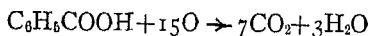


Figure 3

*Materials* { 2 grams of benzoic acid  
5 grams of cupric oxide  
Solution of calcium hydroxide (1 gram treated with  
50 cc. of water and filtered)

*Procedure.* Arrange an apparatus as shown in the figure. The apparatus is now disconnected and a mixture of cupric oxide and benzoic acid placed in the hard glass test tube *A*; filtered solution of calcium hydroxide is poured into flask *B*; and a small quantity of soda lime is placed in the calcium chloride tube *C*. To prepare the mixture for *A*, heat 5 grams of cupric oxide for a few minutes in a porcelain dish to expel moisture. Then allow the oxide to cool, after which mix one half of it with 2 grams of benzoic acid,  $C_6H_5COOH$ , and place it in the hard glass test tube *A*. The remainder of the cupric oxide is now poured into the tube *A*, on top of this mixture.

Next treat about 1 gram of calcium hydroxide with 50 cc. of water. Filter the solution and pour it into flask *B*. Connect flask *B* with a calcium chloride tube *C*, containing soda lime. The soda lime is placed in the calcium chloride tube in the following manner: Place a small roll of glass wool inside the chloride tube, next to the narrow end. Pour into the tube granulated soda lime until it is about two thirds full, and insert another layer of glass wool. The glass wool prevents the contents from falling out.

The entire apparatus containing the various materials is now adjusted. Heat first the copper oxide and then the mixture of copper oxide and benzoic acid. The hydrogen of the organic compound is oxidized to water, which collects at the exit end of the test tube, while the carbon is converted to carbon dioxide, which forms with the clear limewater a precipitate of calcium carbonate.

## EXPERIMENT 7

### Test for halogens in organic compounds

*Procedure.* Place a piece of calcium oxide (pea size) in a test tube and heat to a rather high temperature. Remove the tube from the flame and add quickly three drops of chloroform,  $CHCl_3$ . Allow the tube to cool; add about 5 cc. of water and a few cubic centimeters of dilute nitric acid to dissolve the contents of the tube. Now add 2 cc. of silver nitrate solution (1:20) and notice that a precipitate of silver chloride is obtained, which shows the presence of chlorine in the chloroform. The water and nitric acid used should be tested with silver nitrate to insure the absence of chlorides in these reagents. Chloroform is a compound containing carbon, hydrogen, and chlorine. When heated with lime it decomposes and the chlorine

unites with the calcium, forming calcium chloride, which later reacts with silver nitrate, forming silver chloride.

NOTE. Read the note on solutions in the Appendix, page 452.

## EXPERIMENT 8

### Test for nitrogen

Mix in a mortar 0.5 gram of urea,  $\text{CO}(\text{NH}_2)_2$ , with about 2 grams of soda lime. Pour the mixture into a test tube, and heat. Notice the odor of the gas which is evolved. Urea is a compound containing carbon, hydrogen, oxygen, and nitrogen. When heated with soda lime decomposition occurs, and the nitrogen and hydrogen of the urea unite, forming ammonia gas, which escapes.

**Quantitative analysis.** When a qualitative analysis of an organic compound has been made and certain elements have been found to be present, a quantitative analysis should then be made to determine the exact amount of each element present. The exact amount of carbon and hydrogen is determined in one experiment by placing a weighed quantity of the compound in a combustion tube which contains copper oxide. Oxygen is passed through the tube, which is heated to a high temperature. The carbon of the compound is oxidized to carbon dioxide, and the hydrogen to water. The carbon dioxide is absorbed in a vessel containing a solution of potassium hydroxide, and the water is absorbed in a tube containing solid calcium chloride. The increase in the weights of the tubes containing potassium hydroxide and calcium chloride enables us to calculate the exact amount of carbon and hydrogen in the organic compound.

Nitrogen may be determined by various means, one of which is called the *Kjeldahl method*. This consists in heating a weighed quantity of the substance with concentrated sulfuric acid. The organic compound is thus decomposed and the nitrogen is converted into ammonium sulfate. The mixture is now treated with a solution of sodium hydroxide and distilled. The ammonia evolved is absorbed in a measured quantity of standard

sulfuric acid. The quantity of sulfuric acid neutralized by ammonia is determined by titration, and from this result the amount of nitrogen in the organic compound may be calculated.

Halogens such as chlorine, bromine, and iodine are determined by oxidizing the compound in a sealed tube with nitric acid in the presence of silver nitrate. The compound is thus decomposed and the carbon is oxidized to carbon dioxide, the hydrogen to water, and the halogen unites with silver, forming the insoluble silver chloride, bromide, or iodide. The tube is now opened, the contents washed out and filtered, and the insoluble silver halide weighed. From the result thus obtained the amount of the halogen present is calculated.

The quantity of oxygen is obtained indirectly by determining the quantity of the other elements present in the compound. The sum of the percentages of the other elements, subtracted from 100, gives the percentage of oxygen.

**Percentage composition.** The qualitative and quantitative analyses of a compound show the elements which are present and also the exact amount of each. This is illustrated by the following example showing the results of the analysis of hexahydro benzene: Hexahydro benzene is an oil which boils at  $81^{\circ}$ ; it is obtained from Russian petroleum. A qualitative analysis of this substance showed that it contained only the elements carbon and hydrogen. A quantitative analysis was now made by oxidizing it in a combustion tube. The compound was thus decomposed, yielding the oxidation products, carbon dioxide and water, which were weighed. The following results were obtained:

0.1054 gram of hexahydro	{	0.3313 gram of carbon dioxide
benzene gave		and
		0.1355 gram of water

From these figures the percentage composition was calculated in the following manner (atomic weights,  $C=12$ ,  $H=1$ ,  $O=16$ ; molecular weights,  $CO_2=44$ ,  $H_2O=18$ ):

CO<sub>2</sub> C

$$44 : 12 = 0.3313 : X$$

X = 0.09035 gram of carbon

$$0.1054 : 0.09035 = 100 : X$$

X = 85.72 per cent carbon

H<sub>2</sub>O H<sub>2</sub>

$$18 : 2 = 0.1355 : X$$

X = 0.01506 gram hydrogen

$$0.1054 : 0.01506 = 100 : X$$

X = 14.28 per cent hydrogen

percentage composition of hexahydro benzene

{	85.72 per cent carbon
	14.28 per cent hydrogen
	100.00 total

**Empirical formula.** When the compound has been analyzed and the exact amount of each element present ascertained, the next step is to calculate the empirical formula. The empirical formula of a compound is the simplest formula calculated from the chemical analysis. It is obtained by dividing the percentage amount of each element in a compound by the atomic weight of that element. The figures thus obtained are converted to the simplest whole numbers by dividing each of them by the one having the lowest value. The method of calculation is illustrated by the following example: The analysis of hexahydro benzene showed that it contained 85.72 per cent carbon and 14.28 per cent hydrogen. The atomic weight of carbon is twelve times the atomic weight of hydrogen, and therefore the ratio between the number of carbon and hydrogen atoms in the compound is obtained by dividing the percentage of each of these elements by their atomic weights:

$$\frac{85.72}{12} = 7.14 \text{ and } \frac{14.28}{1} = 14.28$$

The ratio between the number of carbon and hydrogen atoms is, therefore,

$$\text{carbon atoms : hydrogen atoms} = 7.14 : 14.28$$



Now there cannot be less than one atom of each element in a compound, and the figure representing the number of atoms of an element must always be a whole number. The figures representing the ratio between the number of carbon and hydrogen atoms are converted to the simplest whole numbers by dividing each of them by the one having the lowest value,

$$\frac{7.14}{7.14} = 1 \text{ and } \frac{14.28}{7.14} = 2$$

The compound contains twice as many hydrogen atoms as carbon atoms, and the simplest, or empirical, formula is therefore  $\text{CH}_2$ . The results of the analysis of hexahydro benzene and of this method of calculation applied to these results are summarized in the following table:

ELEMENTS	PERCENTAGE COMPOSITION	ATOMIC WEIGHT		SIMPLEST WHOLE NUMBERS REPRESENTING THE RATIO BETWEEN THE NUMBER OF ATOMS IN THE MOLECULE
Carbon	85.72	12	$\frac{85.72}{12} = 7.14$	$\frac{7.14}{7.14} = 1$
Hydrogen	14.28	1	$\frac{14.28}{1} = 14.28$	$\frac{14.28}{7.14} = 2$

If the compound contained other elements in addition to carbon and hydrogen, the results would be calculated in a similar manner.

The empirical formula represents an atomic ratio and shows only the relative number of atoms in the molecule. In the example we have given, the empirical formula calculated from the analysis shows that the compound contains twice as many hydrogen atoms as carbon atoms, but it does not show the exact number of carbon and hydrogen atoms in the compound. Any multiple of the empirical formula, such as  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_4\text{H}_8$ ,

$C_5H_{10}$ ,  $C_6H_{12}$ , and  $C_7H_{14}$ , would represent the compound equally as well as the simplest formula  $CH_2$ , since in all these formulas the number of hydrogen atoms is double the number of carbon atoms. It is evident that the results of our analysis do not enable us to determine the exact formula of this compound.

Now the empirical formula and each of its multiples have a definite molecular weight as represented below :

$CH_2$	$C_2H_4$	$C_3H_6$	$C_4H_8$	$C_5H_{10}$	$C_6H_{12}$	$C_7H_{14}$
14	28	42	56	70	84	98

To determine which empirical formula is the true formula, we must determine in another experiment the molecular weight of this compound which we have already analyzed.

**Molecular weight.** The molecular weight of a compound that can be converted into a gas without decomposition is conveniently calculated from the vapor density of the compound. The vapor density of a compound is the weight of a given volume of that compound as compared to the weight of an equal volume of some substance accepted as a standard. Figures showing the vapor densities of various compounds represent the relative weights of equal volumes of those substances.

The vapor density is conveniently determined by Victor Meyer's method, which consists in converting a weighed amount of a compound, either a solid or a liquid, into a gas and measuring

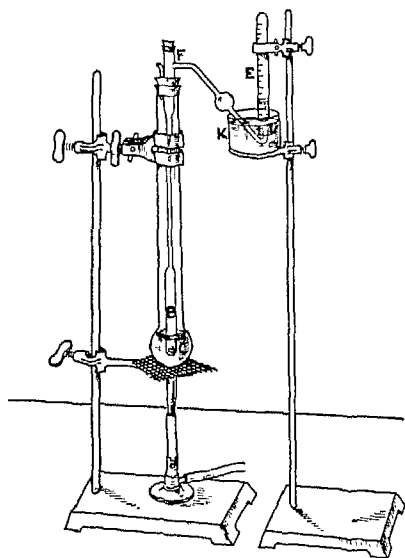


Figure 4

the volume of gas obtained. A diagram of the apparatus is shown above, in Figure 4.

The water in *C* is boiled, and as a result a portion of the air in *B* is expelled, the bubbles escaping into the tank *K*. When no more air issues from *B*, the eudiometer *E*, used for measuring gases, is filled with water and placed over the exit end of *B*.

The stopper at *F* is removed and a small bulb containing a weighed amount of the compound whose molecular weight is desired is dropped into *B*, and the stopper quickly replaced. The substance is thus converted into a vapor, and a portion of the air in *B*, equal to the volume of the compound which has thus been converted into a gas, is expelled into *E*. The eudiometer containing the gas is now transferred to a large cylinder of water and so placed that the water on the inside of the eudiometer is at the same level as the water in the cylinder, as shown in Figure 5.

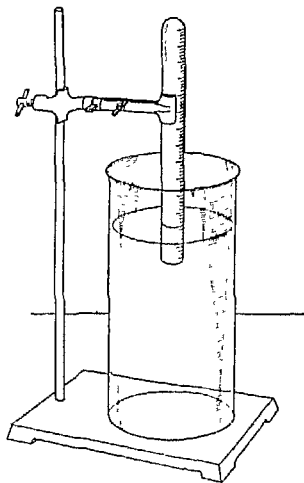


Figure 5

The gas is now under atmospheric pressure, which is ascertained by reading the barometer. The observed volume of gas must now be reduced to the standard conditions of temperature and pressure according to the following formula :

$$V = v \times \frac{B - W}{760} \times \frac{273}{273 + t}$$

In the formula above,

*V* = Corrected volume of gas at 0° and 760 mm.

*v* = Observed volume of gas.

*B* = Barometric reading corrected for temperature.

*W* = Aqueous tension.

*t* = Temperature of the laboratory at the time of the experiment.

A weighed quantity of hexahydro benzene was converted into a gas in accordance with the procedure explained above, and the volume of gas thus obtained was reduced to the standard conditions of temperature and pressure. The following results were obtained:

0.0705 gram of hexahydro benzene when converted to a gas measured 18.8 cc.

1 cc. of hexahydro benzene gas weighs  $\frac{0.0705}{18.8} = 0.00375$  gram.

1000 cc. of hexahydro benzene gas weigh 3.75 grams.

The standard adopted for atomic weights is oxygen=16 ( $O=16$ ), and for molecular weights oxygen=32 ( $O_2=32$ ), because a molecule of oxygen contains two atoms. One liter of oxygen under standard conditions of temperature and pressure ( $0^\circ$  and 760 mm.) weighs 1.429 grams.

$$\frac{\text{Weight of one liter of hexahydro benzene}}{\text{Weight of one liter of oxygen}} = \frac{3.75}{1.429} = 2.624$$

The vapor density of hexahydro benzene compared to oxygen as a standard is 2.624, which means that one liter of hexahydro benzene weighs 2.624 times the weight of one liter of oxygen.

According to Avogadro's hypothesis, equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules, and consequently if we determine the weights of equal volumes of gases we know the relative weights of the molecules in those gases. Since 32 is the adopted molecular weight of oxygen, then the molecular weight of hexahydro benzene is  $2.624 \times 32 = 84$ .

The molecular weight of hexahydro benzene could also be calculated in another manner: Since one liter of oxygen weighs 1.429 grams and 32 is the adopted molecular weight of oxygen, then  $\frac{32}{1.429} = 22.4$ ; consequently 22.4 liters of oxygen weigh 32 grams, and the weight of 22.4 liters of any other gas will be the

molecular weight of that gas. Now one liter of hexahydro benzene gas weighs 3.75 grams, and 22.4 liters weigh  $3.75 \times 22.4 = 84$ , which is the molecular weight of hexahydro benzene.

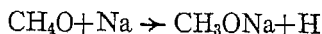
There are various other methods, such as the lowering of the freezing point or rise in the boiling point, which are used to determine molecular weights.

**Molecular formula.** As previously explained, the simplest formula of hexahydro benzene calculated from the analysis is  $\text{CH}_2$ . This formula shows that in a molecule of hexahydro benzene there are twice as many hydrogen atoms as carbon atoms. Any multiple of the simplest formula may be the true formula. Since each empirical formula has its own molecular weight, we can ascertain which empirical formula is the true molecular formula by determining in a separate experiment the molecular weight of hexahydro benzene. As we have seen, the molecular weight of hexahydro benzene determined by the vapor density method of Victor Meyer is 84. Since the molecular weight of hexahydro benzene as determined by experiment agrees with the molecular weight (84) of the empirical formula  $\text{C}_6\text{H}_{12}$ , then  $\text{C}_6\text{H}_{12}$  is the true molecular formula of hexahydro benzene.

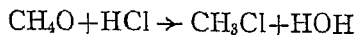
In determining the molecular formula of a compound which can be converted into a gas without decomposition, an outline of the procedure, as we have already explained, is as follows:

1. Analysis.
2. Calculation of percentage composition.
3. Calculation of the empirical formula and its molecular weight, and also the molecular weights of several multiples of the empirical formula.
4. Determination of the vapor density and calculation of the molecular weight of the compound.
5. Determination of the true molecular formula by comparing the molecular weight of the compound as determined by experiment with the calculated molecular weights of the various empirical formulas.

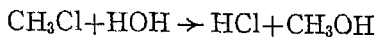
**Structural formula.** A molecular formula, such as  $\text{H}_2\text{SO}_4$ ,  $\text{C}_2\text{H}_6\text{O}$ , and  $\text{C}_6\text{H}_{12}$ , shows simply the composition of these compounds and their molecular weights. In organic chemistry we frequently find two compounds which have the same molecular formula but which are different in their physical and chemical properties. The difference in the behavior of such compounds is probably due to a different arrangement of the atoms within the molecule. By studying the chemical behavior of organic compounds, — that is, the reactions by which they can be prepared and their decompositions under the influence of various reagents, — it is possible to obtain some idea of the manner in which the atoms are combined within the molecule. These facts may be expressed in the form of a structural, or constitutional, formula which represents the general chemical behavior of the compound. For instance, methyl alcohol has the molecular formula  $\text{CH}_4\text{O}$ . When treated with sodium the following reaction takes place:



One atom of sodium enters the molecule of methyl alcohol and takes the place of one atom of hydrogen which is given off. The other three atoms of hydrogen in the alcohol are unaffected. When methyl alcohol is treated with gaseous hydrogen chloride, one atom of hydrogen and one atom of oxygen leave the compound, while one atom of chlorine enters it. The products of the reaction are methyl chloride,  $\text{CH}_3\text{Cl}$ , and water:



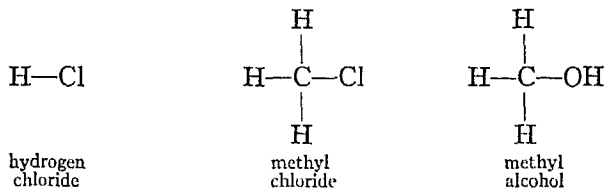
When methyl chloride is hydrolyzed in the presence of a large amount of water, the above reaction is reversed, and we obtain from methyl chloride the products hydrogen chloride and methyl alcohol:



In view of the evidence gained from the above experiments, it is customary to write the formula of methyl alcohol,  $\text{CH}_3\text{OH}$ , which shows that one atom of hydrogen is not situated in the

molecule in the same manner as the other three atoms of hydrogen. Moreover, this particular hydrogen atom is united to the oxygen, since the two can be displaced by chlorine.

The structural formulas of organic chemistry present to one familiar with them considerable information based upon laboratory experiments. A structural, or constitutional, formula expresses, then, not only the composition and relative molecular weight of a compound, but also the atomic arrangement within the molecule. The usefulness of such formulas is based upon the assumption that the chemical properties of a compound are determined by the arrangement of the atoms within the molecule. A structural formula as ordinarily written represents a molecule as composed of atoms which are linked together by hyphens in a particular manner. These formulas are written in accordance with the valency of the elements composing the molecule and information gained from laboratory experiments. For instance, the structural formula of the following compounds would be :



It is important for the student to bear in mind that a constitutional formula does not represent the actual physical structure of a molecule. It is simply a diagram representing the general chemical behavior of the compound.

**Radicals.** In the reaction  $\text{CH}_3\text{Cl} + \text{HOH} \rightarrow \text{HCl} + \text{CH}_3\text{OH}$  we observe that we have on one side of our equation the compound methyl chloride,  $\text{CH}_3\text{Cl}$ , which contains the  $(\text{CH}_3)$  group of atoms, and on the other side methyl alcohol,  $\text{CH}_3\text{OH}$ , containing the same group. A group of atoms such as the methyl group  $(\text{CH}_3)$  which passes unchanged from one compound to another in a chemical reaction is called a *radical*. A radical, then, is

simply that part of a compound which remains unchanged and acts as a single atom in chemical transformations. We shall become familiar with a number of organic radicals which we shall meet in the course of our study.

**Classification of carbon compounds.** The simplest carbon compounds are the hydrocarbons, which contain only carbon and hydrogen. There are a number of different series of these hydrocarbons, but only a few are of sufficient importance to demand the attention of a beginner. By treating these hydrocarbons with various reagents a number of classes of hydrocarbon derivatives may be obtained, such as the halogen derivatives or the alcohols. However, the relations between a given hydrocarbon and its derivatives are very similar to the relations between another hydrocarbon and its derivatives. As a result of laboratory experimentation a large number of compounds have been discovered. These compounds are usually classed in two main divisions, the *aliphatic hydrocarbons* and derivatives, and the *aromatic hydrocarbons* and derivatives.

The word *aliphatic* is from a Greek word meaning "fat," and was originally used as a general name for the first main division of organic compounds because the substances known as fats are members of this division. The second main division was called *aromatic* because many of the compounds in this division have a fragrant odor. Although many of the aliphatic compounds are not directly related to the fats and many of the aromatic compounds do not have a fragrant odor, this classification is still used because in certain respects the general chemical properties of these two main divisions are somewhat different.



## QUESTIONS

1. What was Wöhler's discovery (1828), and what was the importance of it?
2. State some of the natural sources of carbon compounds.
3. How are liquid and solid organic compounds purified, and how is the purity of these compounds determined?
4. A certain compound boils at  $112^{\circ}$ . When the crude compound was distilled, the following fractions were collected:  $100^{\circ}$ – $108^{\circ}$ ,  $108^{\circ}$ – $116^{\circ}$ ,  $116^{\circ}$ – $124^{\circ}$ . Which fraction contains the largest amount of the pure compound?
5. Name some of the principal organic solvents; do they boil at temperatures below  $100^{\circ}$ , and are they inflammable?
6. Name some of the elements frequently present in organic compounds.
7. How do you detect the presence of the following elements in organic compounds: carbon, hydrogen, chlorine, and nitrogen?
8. What is meant by the qualitative and quantitative analyses of organic compounds?
9. What is meant by the percentage composition of a compound?
10. How is the empirical formula of a compound determined?
11. What is meant by the vapor density of a compound, and how is it determined by Victor Meyer's method?
12. How is the molecular weight of a compound determined?
13. How does Avogadro's hypothesis apply in determining molecular weights, and why is the figure 22.4 used?
14. What is the difference between an empirical and a molecular formula?
15. A certain compound when analyzed gave 10.04 per cent carbon, 0.84 per cent hydrogen, and 89.12 per cent chlorine ( $C=12$ ,  $H=1$ ,  $Cl=35.5$ ). When converted to a gas, the weight of 22.4 liters of this substance was 119 grams. Calculate the molecular formula.
16. The analysis of a certain substance gave 12.77 per cent carbon, 2.12 per cent hydrogen, and 85.11 per cent bromine ( $C=12$ ,  $H=1$ ,  $Br=80$ ). The vapor density of this compound compared to oxygen as a standard is 5.873. Calculate the molecular formula.
17. What is meant by a structural formula, and how is it determined?
18. Explain, with examples, what is meant by radicals.
19. Into what two general classes are organic compounds divided?

## CHAPTER TWO

### PARAFFIN HYDROCARBONS AND HALOGEN DERIVATIVES

THE first series of aliphatic hydrocarbons is called the *paraffins* because some of the higher members of this series are contained in paraffin wax. In the following table are given a few of the simpler members of this series :

PARAFFIN HYDROCARBONS

NAME	FORMULA	BOILING POINT, °C.
Methane . . . . .	$\text{CH}_4$	-164
Ethane . . . . .	$\text{C}_2\text{H}_6$	-93
Propane . . . . .	$\text{C}_3\text{H}_8$	-45
Butane . . . . .	$\text{C}_4\text{H}_{10}$	1
Pentane . . . . .	$\text{C}_5\text{H}_{12}$	36.4
Hexane . . . . .	$\text{C}_6\text{H}_{14}$	71
Heptane . . . . .	$\text{C}_7\text{H}_{16}$	99

By adding  $\text{CH}_2$  to the formula of any member of this series, we obtain the formula of the following member. Each compound, therefore, differs from the preceding one by a  $\text{CH}_2$  group. A series of this kind is known as a *homologous series*. Many of these compounds are found in petroleum, an oil which occurs in the United States, Russia, and other parts of the world. As to their chemical properties, they are not readily acted upon by reagents such as nitric or sulfuric acid. They react, however, with chlorine and bromine. The first member of this series, **methane** (marsh gas),  $\text{CH}_4$ , is formed in marshes by the de-

composition of vegetable matter under water. Fire damp, a gas which occurs in coal mines, contains about 80 per cent of methane. The explosions in coal mines are caused by the ignition of methane. It may be prepared in the laboratory by various methods.

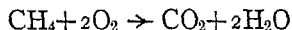
## EXPERIMENT 9

Preparation of methane,  $\text{CH}_4$ 

*Materials*  $\left\{ \begin{array}{l} 2 \text{ grams of dehydrated sodium acetate} \\ 7 \text{ grams of soda lime} \end{array} \right.$

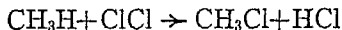
*Procedure.* Place 2 grams of dehydrated sodium acetate,  $\text{CH}_3\text{COONa}$ , and 7 grams of dry soda lime in a mortar and grind the mixture thoroughly by means of a pestle. Pour the mixture upon a piece of paper. Lift up the paper, bend it somewhat, and using it as a kind of scoop gradually slide the mixture into a hard glass test tube. The test tube is now clamped to an iron stand and heated by flames from two Bunsen burners or by one burner giving a large flame. When gas appears at the mouth of the test tube, apply a lighted match and notice if it burns.

In preparing methane, more satisfactory results are obtained if soda lime is used instead of pure sodium hydroxide. Soda lime is prepared by heating a mixture of two parts of slaked lime with one part of sodium hydroxide. Methane prepared by the method above contains volatile impurities which may be observed. In pure condition, however, methane is a colorless gas which burns easily:

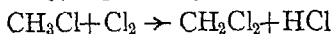


When mixed with air in the proper proportion, it forms an explosive mixture.

*Substitution.* When methane is treated with chlorine, substitution occurs and one atom of hydrogen is replaced by one atom of chlorine:



The interaction of methane and chlorine is, then, a substitution reaction. By the continued action of chlorine on methane all the hydrogen atoms are replaced, or substituted, by chlorine :



Methane reacts with bromine in a similar manner, yielding similar substitution products. Write the equations.

**Nomenclature.** The compound  $\text{CH}_3\text{Cl}$  is a hydrocarbon derivative of methane and is called *monochlor methane*. It may be regarded as methane in which one atom of hydrogen has been substituted by one atom of chlorine. It is therefore a monosubstitution derivative of methane. Just as  $\text{HCl}$  consists of one atom of hydrogen united to one atom of chlorine and is called *hydrogen chloride*, so  $\text{CH}_3\text{Cl}$  consists of the methyl radical ( $\text{CH}_3$ ) united to one atom of chlorine, and consequently it is called *methyl chloride*. The compound  $\text{CH}_3\text{Cl}$  is known, then, by two names, *methyl chloride* and *monochlor methane*. The compound  $\text{CH}_2\text{Cl}_2$  is called *methylene dichloride* because it contains the methylene ( $\text{CH}_2$ ) group. It is also called *dichlor methane* and may be regarded as a disubstitution product of methane; that is, methane in which two hydrogen atoms have been substituted by two atoms of chlorine.

The compound  $\text{CHCl}_3$  is known as *chloroform*. It is a valuable anesthetic and is used extensively in medical work. Chloroform is also called *trichlor methane*, because it is a trisubstitution product of methane. The substance  $\text{CCl}_4$  is called *tetrachlor methane*, or *carbon tetrachloride*. It is used considerably as a solvent for organic compounds. It frequently happens that a compound may have two or more names. If the student endeavors to understand the reason for each name, he is more likely to remember it. The compounds methyl chloride,

methylene chloride, chloroform, and carbon tetrachloride are colorless oils having boiling points below  $100^{\circ}$ . Although they are formed by the interaction of methane and chlorine, it would be difficult to obtain them in pure condition by this method, because a mixture of compounds is obtained which are difficult to separate. There are, however, certain indirect methods of preparation which enable us to obtain these halogen derivatives of methane in pure condition.

**Saturated compounds.** The valence of an element is the ability of one atom of that element to unite with one atom of hydrogen or with another element of the same combining capacity, forming a stable compound. The valence of carbon is four, as shown by the formulas of the paraffin hydrocarbons ( $\text{CH}_4$ ) and their halogen derivatives ( $\text{CH}_3\text{Cl}$ ). These paraffin hydrocarbons and their halogen derivatives are saturated compounds and can react only by substitution. As shown by the reactions above, if an atom of chlorine enters a saturated compound such as methane,  $\text{CH}_4$ , then an atom of hydrogen must leave methane because the valence of carbon is only four and one carbon atom can hold only four univalent atoms in combination. In a saturated compound the maximum combining capacity of the carbon atom is utilized and one of the hydrogen atoms must be give off if another atom like chlorine enters the molecule. Saturated compounds, then, can react only by substitution.

**Outline equations.** As shown by the equations above, carbon tetrachloride may be prepared from methane by a series of reactions. Instead of balancing each equation separately, it is often more convenient in organic chemistry to write the series of reactions in outline, showing the starting point, reagents used, the intermediate products, and the final products, as follows:



By means of this method of writing equations a considerable amount of information can be expressed in a small space, which

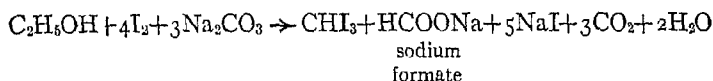
is often very desirable when we consider compounds having more complicated formulas.

The paraffins do not react directly with iodine. However, iodine derivatives may be formed by indirect methods or special reactions. For instance, iodoform,  $\text{CHI}_3$ , may be prepared conveniently from ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , by treating it with iodine in the presence of a carbonate or hydroxide.

#### EXPERIMENT 10

##### Preparation of iodoform, $\text{CHI}_3$

(Triiodo methane)



*Materials*  $\left\{ \begin{array}{l} 15 \text{ grams crystallized sodium carbonate} \\ 75 \text{ cc. water} \\ 7.5 \text{ cc. ethyl alcohol (95 per cent)} \\ 7.5 \text{ grams iodine} \end{array} \right.$

*Procedure.* In a 200 cc. beaker, heat 75 cc. of water to a temperature of  $70^\circ$  and regulate the flame so as to maintain the water at about this temperature. Introduce into the warm water 15 grams of powdered, crystallized sodium carbonate. Stir until the carbonate is dissolved. Now add 7.5 cc. of ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$  (95 per cent), stir, and add gradually 7.5 grams of powdered iodine. The iodine should be finely powdered and added occasionally in small quantities so that the solution will have a light-yellow color, showing that the iodine is dissolving readily. A very dark-colored solution shows that too much iodine has been added. In such a case discontinue the addition of the iodine and stir until the excess of iodine is dissolved and a light-yellow-colored solution is obtained, and then continue the addition of the iodine. Yellow crystals of iodoform separate from the solution.

Filter and wash the crystals on the filter paper with a little water. Recrystallize in the following manner: Immerse a beaker containing about 20 cc. of ethyl alcohol in a water bath previously heated to about  $80^\circ$ . On account of the inflammability of alcohol, do not have a flame under the water bath while the alcohol is being heated. When

the alcohol has become hot, remove the beaker containing it from the water bath. Scrape the iodoform crystals from the filter paper with a spatula and place them in the hot alcohol. Stir the mixture a few minutes and filter from undissolved impurities. Add water to the filtrate until all the iodoform is again precipitated. Filter, and by means of a spatula place the crystals upon pieces of sheet filter paper and allow to dry. When the crystals are thoroughly dry, determine the melting point (Experiment 3).

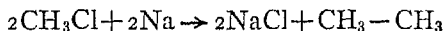
Preserve a specimen of iodoform in accordance with the procedure explained below.

Iodoform crystallizes in six-sided yellow plates, melts at  $119^{\circ}$ , and has a peculiar, characteristic odor. It is used in medicine and surgery as an antiseptic. It is a triiodo substitution product of methane; that is, it may be regarded as methane,  $\text{CH}_4$ , in which three hydrogen atoms have been replaced by three atoms of iodine,  $\text{CHI}_3$ .

**Preservation of crystalline organic compounds.** Crystalline organic compounds may be preserved in bottles which are stoppered securely, or they may be kept in sealed tubes.

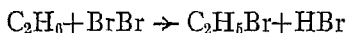
Preserve a specimen of iodoform in the following manner: A soft glass tube 0.5 cm. in diameter and about 14 cm. in length is sealed at one end and cooled. The iodoform is then introduced into the tube. The tube is now heated near the open end, drawn out, and sealed. A label containing the formula and name of the compound is placed on the tube.

**Ethane**,  $\text{C}_2\text{H}_6$ , is the second hydrocarbon of the paraffin series. It may be prepared by the interaction of methyl chloride and sodium (Wurtz's reaction):

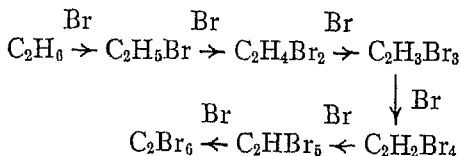


As shown by the equation, the chlorine in methyl chloride is taken up by the sodium, while the two methyl groups unite, forming dimethyl,  $\text{CH}_3 - \text{CH}_3$ , which is ethane,  $\text{C}_2\text{H}_6$ . Write the empirical formula of ethane. Ethane is a gas and reacts

with chlorine or bromine, yielding by substitution reactions halogen derivatives of ethane:



The compound  $\text{C}_2\text{H}_5\text{Br}$  is called *monobrom ethane*. Since it consists of the ethyl radical ( $\text{C}_2\text{H}_5$ ) united to one atom of bromine, it is also called *ethyl bromide*. As in the case of methane, it is difficult to treat ethane with bromine and keep the bromination process exactly under control; consequently, if the bromine treatment is continued long enough a mixture of bromine derivatives of ethane is produced, as shown by the following outline equations:



Balance each of these outline equations.

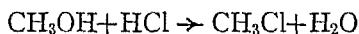
The names of these various bromine derivatives are as follows:

- $\text{C}_2\text{H}_5\text{Br}$ , monobrom ethane or ethyl bromide,
- $\text{C}_2\text{H}_4\text{Br}_2$ , dibrom ethane or ethylene dibromide,
- $\text{C}_2\text{H}_3\text{Br}_3$ , tribrom ethane,
- $\text{C}_2\text{H}_2\text{Br}_4$ , tetrabrom ethane,
- $\text{C}_2\text{HBr}_5$ , pentabrom ethane,
- $\text{C}_2\text{Br}_6$ , hexabrom ethane or perbrom ethane.

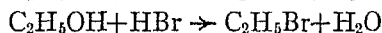
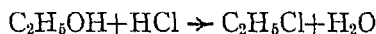
Hexabrom ethane is a solid which decomposes at about  $200^\circ$ , while the other bromine derivatives are liquids which boil at temperatures below  $200^\circ$ . Write the formulas of the corresponding chlorine compounds. Name them, and show by outline reactions how they could be prepared from ethane. The monohalogen derivatives, such as methyl chloride, ethyl chloride, and ethyl bromide, are conveniently prepared by the interaction of the corresponding alcohols with the proper halogen acids. Thus



the interaction of methyl alcohol,  $\text{CH}_3\text{OH}$ , and hydrogen chloride yields methyl chloride,  $\text{CH}_3\text{Cl}$ :



In a similar manner ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ , or ethyl bromide,  $\text{C}_2\text{H}_5\text{Br}$ , may be obtained from ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ :

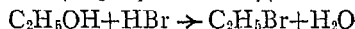
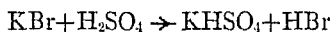


Ethyl bromide is prepared conveniently in the laboratory by the interaction of potassium bromide, sulfuric acid, and ethyl alcohol.

#### EXPERIMENT 11

##### Preparation of ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$

(Monobrom ethane)



*Materials*  $\left\{ \begin{array}{l} 45 \text{ grams potassium bromide} \\ 50 \text{ cc. ethyl alcohol (95 per cent)} \\ 50 \text{ cc. concentrated sulfuric acid} \\ 35 \text{ cc. ice water} \end{array} \right.$

*Procedure.* Pour 50 cc. of concentrated sulfuric acid into a round 300 cc. distilling flask. Add 50 cc. of ethyl alcohol (95 per cent) gradually to the acid, with constant shaking and cooling. The cooling may be effected by allowing tap water to flow on the outside of the flask. Continue to cool, and add gradually 35 cc. of ice water. Forty-five grams of powdered potassium bromide are now added to the mixture, and the flask connected to a condenser. The exit end of the condenser is fitted with an adapter, which is allowed to dip slightly under the surface of about 80 cc. of ice water contained in an Erlenmeyer flask that is immersed in ice water. A diagram of the apparatus is shown in Figure 6. The flask containing the mixture is heated on a wire gauze. If the foaming which occurs sometimes during the action becomes too violent, temporarily discontinue the distillation and remove the receiver. When the foaming has subsided, replace the receiver and continue heating the mixture. The distillation should be continued until no more oily drops of ethyl bromide pass over.

Put a small amount of burette grease on the stopcock of a clean separating funnel so that it may turn easily and will not "stick."

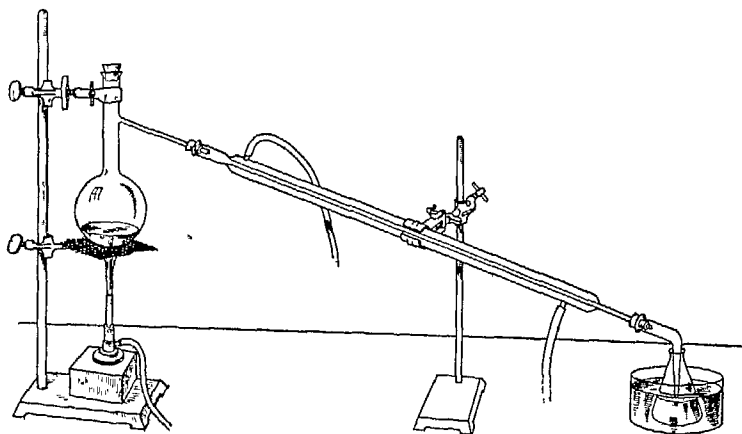


Figure 6

The distillate is now removed and poured into the separating funnel and the lower layer of ethyl bromide separated. The top aqueous layer is thrown away. The ethyl bromide is again poured into the funnel, and to it is added an equal volume of a sodium carbonate solution (1:10). This is to neutralize any acid substances which may have distilled over with the ethyl bromide. The ethyl bromide is separated, again poured into the funnel, shaken with water, and separated again. The bromide is still contaminated with a small quantity of water, which renders the oil turbid. Pour it into a clean, dry Erlenmeyer flask and add about six lumps (pea size) of anhydrous calcium chloride; stopper the flask securely and allow it to remain several hours until the dehydration is complete and the oil is clear. Filter into a distilling flask, distil on a water bath, and collect the fraction boiling between  $35^{\circ}$  and  $43^{\circ}$ .

Ethyl bromide is a colorless oil which boils at  $39^{\circ}$  and has a specific gravity of 1.47 at  $15^{\circ}$ . Preserve a specimen of ethyl bromide in a sealed tube in the manner explained below.

**Preservation of liquid organic compounds.** Liquid organic compounds may be preserved in glass-stoppered bottles or in sealed tubes in the following manner: A soft glass tube about

0.5 cm. in diameter and 16 cm. in length is sealed at one end and allowed to cool. The liquid compound is now poured into the tube until it is about one third full. A rubber tube about 30 cm. in length is connected to the open end of the tube. The glass tube is now heated near the open end, carefully drawn out somewhat, and sealed as shown in Figure 7. The object of using the rubber-tube connection is to prevent the vapors of ethyl bromide from taking fire.

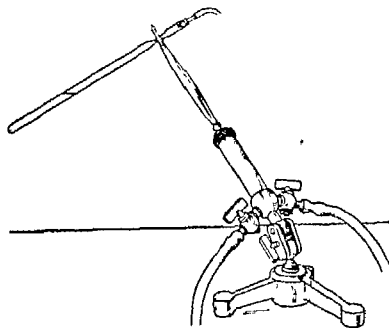
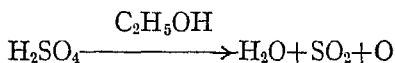


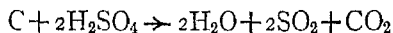
Figure 7

**Calculation of the yield.** The mechanism by which organic compounds are prepared in the laboratory is often somewhat more complicated than the chemical equations would seem to indicate. The reason for this is that the main reaction is often accompanied by side reactions, and consequently a mixture of compounds is often obtained containing a comparatively large amount of one constituent and small amounts of other constituents. In preparing organic compounds, the materials are mixed in the proper proportions and the experiments are performed in a manner that will produce as much of the desired compound as possible and as little of the by-products. In the preparation of ethyl bromide, for instance, all the alcohol used is not converted into the bromide, but a part of it is oxidized by the sulfuric acid, which when heated with organic compounds acts to some extent as an oxidizing agent and is itself reduced :

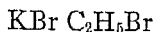


The reaction mixture generally darkens in color when heated, and frequently a quantity of carbonaceous matter is formed.

The carbonaceous matter also reduces a portion of the sulfuric acid, yielding various gases:



A small portion of the alcohol and sulfuric acid are decomposed and are no longer present, and therefore cannot react to form ethyl bromide. The actual yield of ethyl bromide is therefore less than the theoretical yield calculated in accordance with the equations. It is usually customary in making compounds to calculate the theoretical amount of the compound which should be produced according to the equations; then, having made the compound in the laboratory, weigh the actual yield obtained and calculate what per cent that is of the theoretical (100 per cent) yield. For instance, in the preparation of ethyl bromide according to the equations one molecule of potassium bromide should produce one molecule of ethyl bromide. Since 45 grams of potassium bromide were used, then according to the following calculation 41.1 grams of ethyl bromide should be obtained:



$$119 : 108.9 = 45 : x$$

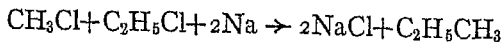
$$x = 41.1$$

In actual practice, however, only about 33 grams of ethyl bromide are obtained, and consequently the yield is only 80 per cent of the amount that theoretically should be obtained:

$$\frac{33}{41.1} \times 100 = 80 \text{ per cent}$$

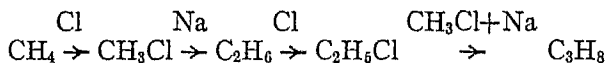
When a student has prepared and purified a compound, he should weigh it and calculate the yield he has obtained.

**Propane**,  $\text{C}_3\text{H}_8$ , is the third member of the paraffin hydrocarbons. It may be prepared by the interaction of methyl chloride, ethyl chloride, and sodium:



Propane is a gas resembling methane and ethane in its chemical behavior. It reacts with chlorine, giving monochlor propane. Write the equation.

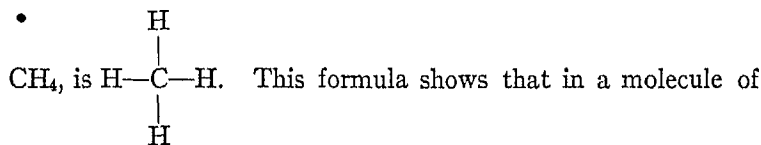
**Synthetic chemistry.** As we have seen, methyl chloride,  $\text{CH}_3\text{Cl}$ , may be obtained from methane. The interaction of methyl chloride and sodium yields ethane,  $\text{C}_2\text{H}_6$ . Ethane treated with chlorine yields ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ . When ethyl chloride is treated with methyl chloride and sodium, it is converted into propane,  $\text{C}_3\text{H}_8$ . These changes are illustrated by the following outline reactions:



Balance each of the outline reactions above. Since the higher hydrocarbons yield derivatives similar to methane, it is possible to build up in the laboratory complex compounds from simple ones. This process is called *synthesis*. It is very interesting and important because, when we have prepared the higher complex compounds, we can proceed to study their physical, chemical, medicinal, and industrial properties. Methods of synthetic chemistry have been extremely helpful in enabling us to discover new compounds, many of which have been used very successfully in the treatment of certain diseases, while others have been used in industrial chemistry for practical purposes such as the manufacture of synthetic dyes and perfumes.

## STRUCTURE OF THE PARAFFIN HYDROCARBONS

**Structure of methane.** As a result of the large amount of experimental work which has been done in organic chemistry, it appears that the most probable structural formula for methane,

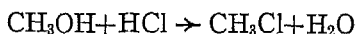


methane the hydrogen atoms are arranged symmetrically around the carbon atom. The molecule of methane is, therefore, supposed to be symmetrical, and all the hydrogen atoms have equal value or bear the same relation to the molecule as a whole. This structural formula is in harmony with the general chemical behavior of methane.

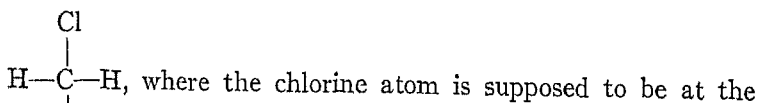
As previously pointed out, when methane is treated with chlorine the first product formed is methyl chloride,  $\text{CH}_3\text{Cl}$ :



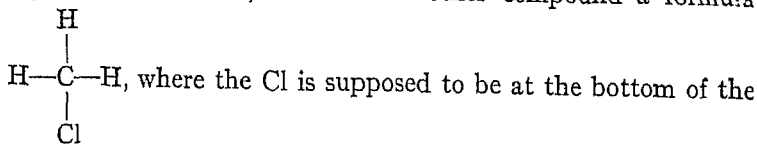
Methyl chloride may also be prepared by treating methyl alcohol,  $\text{CH}_3\text{OH}$ , with gaseous hydrogen chloride:



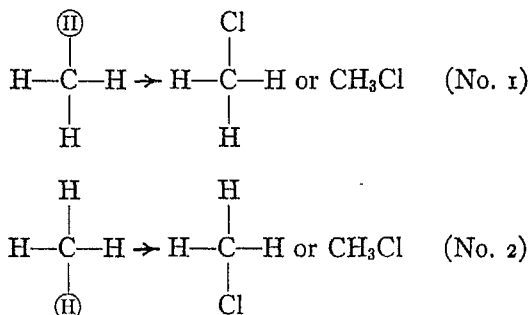
These two methods of preparation do not yield two different kinds of methyl chloride, but, on the contrary, the two methods give the same substance,  $\text{CH}_3\text{Cl}$ , which is a compound of definite physical properties and chemical behavior. It has been demonstrated by laboratory experiments that no matter by what method methyl chloride is prepared, we always obtain exactly the same compound. If it were possible to make two different kinds of methyl chloride by two different methods, then we should have two compounds having the molecular formula  $\text{CH}_3\text{Cl}$ . In order to distinguish these compounds, we should have to assign to them different structural formulas. For instance, we might write for one compound a structural formula



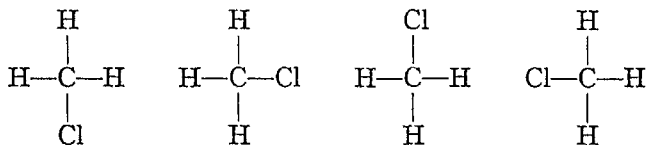
top of the molecule, and for the other compound a formula



molecule. If this were true, then it is evident that the hydrogen atoms in methane would have unequal value, — that is, they would not bear the same relation to the molecule as a whole, — and by substituting chlorine for different hydrogen atoms we could obtain two compounds represented by different structural formulas, as shown by the following equations:



Experimental evidence has shown that methyl chloride may be made in several ways, but the product obtained is always the same substance; there is only one methyl chloride. There is no reason to believe that there is any difference in the hydrogen atoms in methane. When methyl chloride is prepared by the interaction of methane and chlorine, we always obtain the same compound, no matter which one of the hydrogen atoms in methane is replaced by chlorine. Accordingly any one of the following formulas would represent correctly the structure of methyl chloride,  $\text{CH}_3\text{Cl}$ :



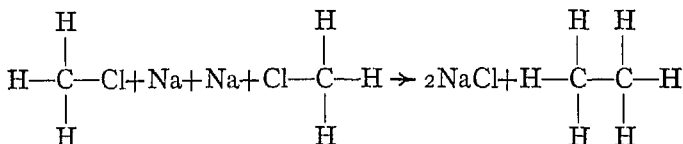
Therefore all the hydrogen atoms in methane have equal value or bear the same relation to the molecule which is represented by the

$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$$

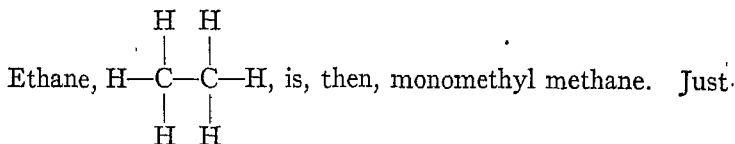
symmetrical formula  $\text{H}-\text{C}-\text{H}$ . Monobrom methane,  $\text{CH}_3\text{Br}$ ,

also has been prepared in various ways, but the same product is always obtained.

**Structure of ethane.** Having decided on a satisfactory structural formula for methane, it is comparatively easy to understand what the structural formula of ethane should be. Since it is formed by the interaction of methyl chloride and sodium, the reaction probably takes place in the following manner:

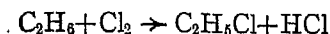


The chlorine in the two molecules of methyl chloride is taken up by the sodium, while the two methyl radicals, which are liberated, unite immediately, forming ethane.



as we can substitute one hydrogen atom in methane by one atom of chlorine, forming monochlor methane, so we can also replace one hydrogen atom by the methyl radical, forming monomethyl methane, which is ethane, as shown by the reaction above. Since ethane consists of the two methyl groups united together, it may also be called *dimethyl*.

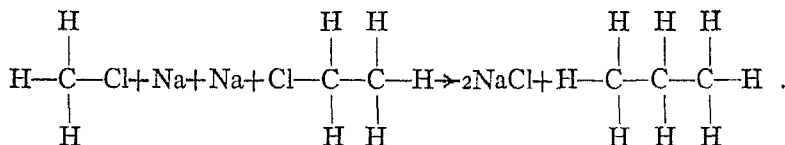
As previously stated, when ethane reacts with chlorine the first product formed is monochlor ethane,  $\text{C}_2\text{H}_5\text{Cl}$ , or ethyl chloride:



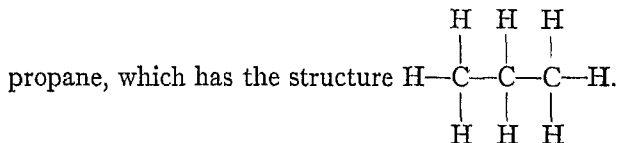


If we had two compounds having the molecular formula  $C_2H_5Cl$ , but different physical and chemical properties, then we should conclude that all the hydrogen atoms in ethane do not have equal value, and by replacing one hydrogen atom by chlorine we should have one ethyl chloride and by substituting a different hydrogen atom by chlorine we should have another ethyl chloride. There are no two compounds having the molecular formula,  $C_2H_5Cl$ , but different physical and chemical properties. We therefore conclude that the molecule of ethane has a symmetrical structure similar to methane, and that in ethane all the hydrogen atoms have equal value or bear the same relation to the molecule.

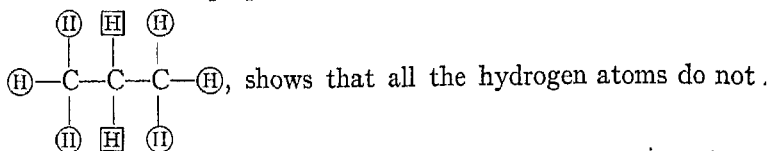
**Structure of propane.** Having decided on satisfactory structural formulas for methane and ethane, formulas which have been worked out in accordance with the information gained from laboratory experiments, we shall now proceed to ascertain what the structural formula of propane should be. Propane may be made by the interaction of ethyl chloride, methyl chloride, and sodium. Writing the equation with complete structural formulas, we should have, then:



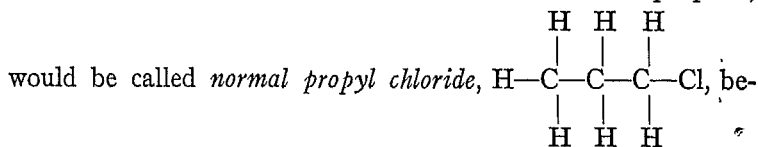
The chlorine atoms in methyl and ethyl chloride unite with sodium, forming sodium chloride, while the methyl and ethyl radicals which are thus liberated unite immediately, forming



**Derivatives of propane.** The structural formula of propane,



have the same value and are not related to the molecule in exactly the same manner. Each one of the hydrogen atoms inclosed in a circle is connected to one carbon atom, which in turn is joined to another carbon atom and two other atoms of hydrogen. Each one of the hydrogen atoms inclosed in a square is joined to a carbon atom, which in turn is connected to two other carbon atoms and to one atom of hydrogen. All the hydrogen atoms, then, which are inclosed in circles are related to the molecule as a whole in the same manner, and all the hydrogen atoms which are inclosed in squares are likewise related to the molecule in the same manner. However, those atoms inclosed in circles are related to the molecule in a manner different from those inclosed in squares. We have, then, two different sets of hydrogen atoms, each of which is situated in a different manner and, therefore, bears a different relation to the molecule. If our formula for propane is correct, we should expect a compound having such a structure to give two different monosubstitution products. For instance, we should expect to be able to make in the laboratory two different monochloro propanes. One of them, obtained by substituting any one of the hydrogen atoms connected to either of the end carbon atoms in propane,



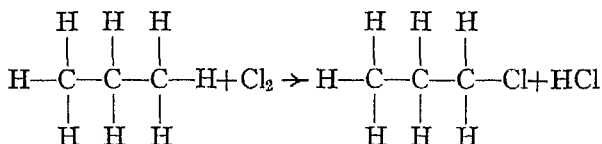
cause it would contain the normal propyl group ( $\text{CH}_3\text{CH}_2\text{CH}_2-$ ), while the other, obtained by substituting either of the hydrogen atoms connected to the middle carbon atom in propane, would

be called *isopropyl chloride*,  $\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ , because it would

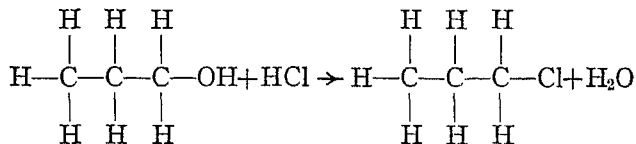
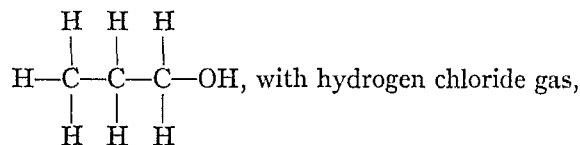
contain the isopropyl group  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 > \text{CH}- \end{array}$ . Both of these compounds have been made in the laboratory.

Normal propyl chloride,  $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Cl} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ , may be obtained

by the interaction of propane and chlorine,



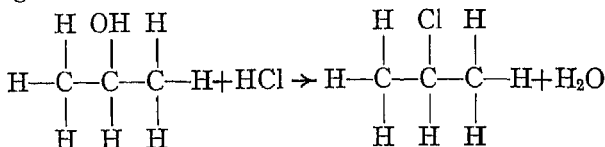
It is also prepared by treating propyl alcohol,



Propyl chloride is a liquid which boils at  $46.5^\circ$ .

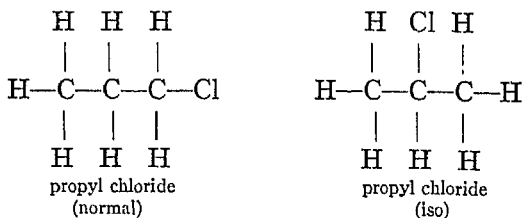
Isopropyl chloride,  $\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ , is prepared by the inter-

action of isopropyl alcohol,  $\begin{array}{c} \text{H} \text{ OH} \text{ H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ , and hydrogen chloride gas:



Isopropyl chloride is a liquid boiling at  $37^\circ$ .

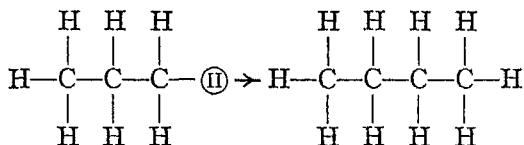
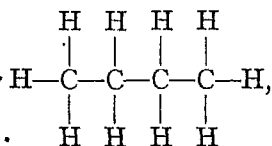
**Isomeric compounds.** The two substances normal propyl chloride and isopropyl chloride have the same molecular formula,  $\text{C}_3\text{H}_7\text{Cl}$ , but their general properties, methods of preparation, and chemical behavior are entirely different. For instance, the boiling point of propyl chloride is  $46.5^\circ$ , while isopropyl chloride boils at  $37^\circ$ . Compounds such as the two propyl chlorides which have the same molecular formula but entirely different physical and chemical properties are called *isomeric compounds*. Such compounds are distinguished by assigning to each of them a different structural formula.



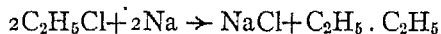
These formulas are written in accordance with the general chemical behavior of these compounds and the methods which are used in preparing them.

**Butanes,  $\text{C}_4\text{H}_{10}$ .** As we have seen, propane contains hydrogen atoms that have two different relations to the carbon atoms in the molecule, and it therefore yields two isomeric monochlor derivatives, which are propyl chloride and isopropyl chloride. Propane

also yields two isomeric monomethyl derivatives, which are normal butane and isobutane. If one of the propane hydrogen atoms which is inclosed in a circle is substituted by a methyl group, we obtain a compound having the formula



This substance is known as *normal butane* and is prepared by the interaction of ethyl chloride and sodium:

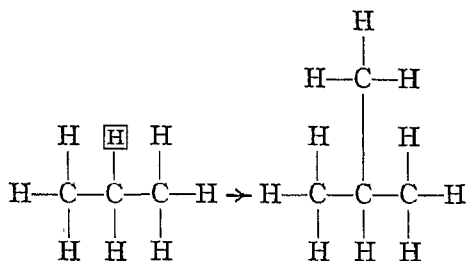


As shown by the equation above, the chlorine in ethyl chloride is taken up by sodium, leaving the two ethyl groups, which unite,

forming diethyl,  $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{C}_2\text{H}_5 \end{array}$  or normal butane,  $\text{C}_4\text{H}_{10}$ . Normal butane

is a gas which may be condensed to a liquid boiling at  $1^\circ$ .

If one of the propane hydrogen atoms inclosed in a square is replaced by a methyl group, a compound is obtained known as *isobutane*:



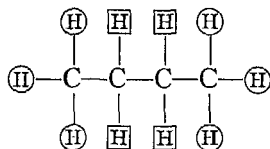
Isobutane,  $\text{CH}(\text{CH}_3)_3$ , is prepared by reducing tertiary butyl iodide (trimethyl iodo methane),  $\text{CI}(\text{CH}_3)_3$ , with hydrogen:



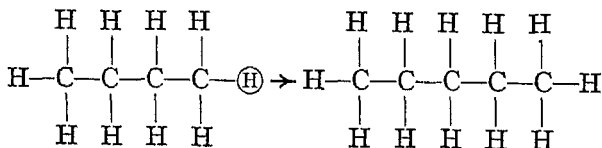
Tertiary butyl iodide may be regarded as methane ( $\text{CH}_4$ ) in which one hydrogen atom has been substituted by one atom of iodine, while the other three hydrogen atoms have been replaced by three methyl groups. This compound reacts with hydrogen by double decomposition, the one atom of iodine being substituted by one atom of hydrogen, as shown by the equation above. Isobutane is a gas which may be condensed to a liquid boiling at  $-17^\circ$ .

We have, then, two butanes,  $\text{C}_4\text{H}_{10}$ , which are isomeric monomethyl derivatives of propane.

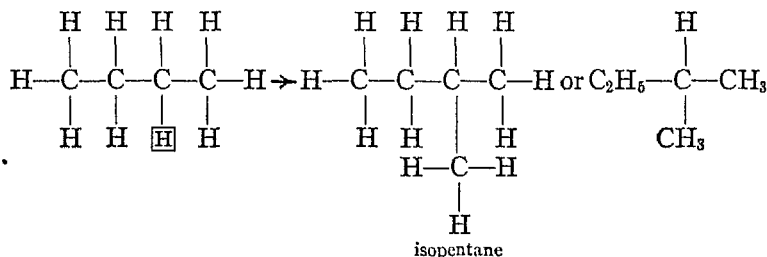
**Pentanes**,  $\text{C}_5\text{H}_{12}$ . Each of the two isomeric butanes, like propane, has hydrogen atoms that have different relations to the carbon atoms in the molecule. These butanes yield monomethyl derivatives known as *pentanes*. In the structural formula of normal butane,



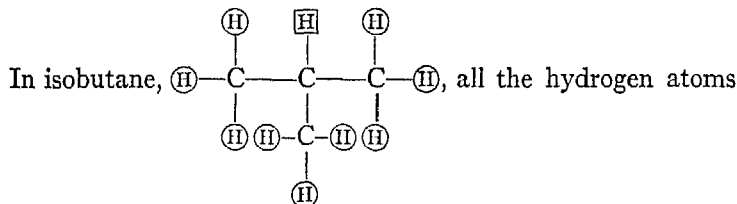
those hydrogen atoms which are inclosed in circles are connected in the molecule in a manner different from those which are inclosed in squares. Consequently normal butane should yield two isomeric monomethyl derivatives having the molecular formula  $\text{C}_5\text{H}_{12}$ . The first one, called *normal pentane*, is obtained by substituting with a methyl group any one of the hydrogen atoms inclosed in circles,



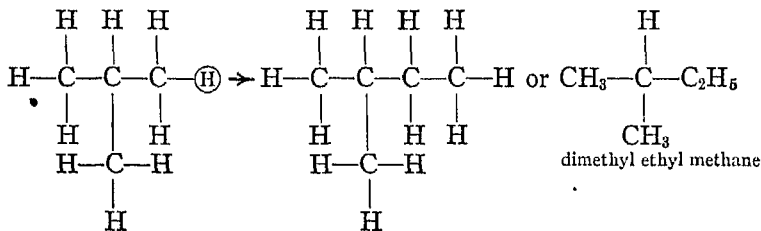
The corresponding isomer, called *isopentane*, is obtained from normal butane by substituting with a methyl group any one of the hydrogen atoms inclosed in squares,

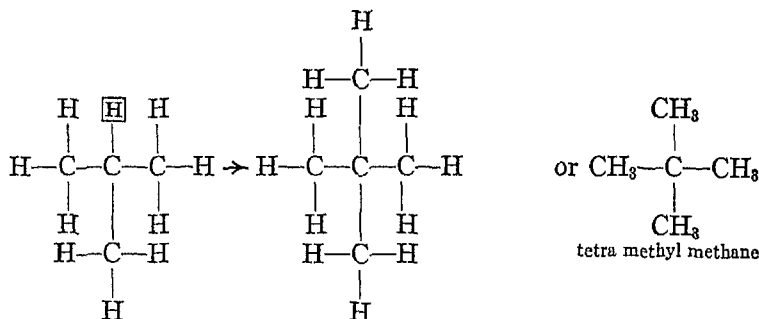


Isopentane may be regarded as derived from methane and is called *dimethyl ethyl methane*.



which are inclosed in circles are related to the molecule in the same manner, while the one hydrogen atom inclosed in a square is connected to the molecule in a manner different from the other hydrogen atoms. We should, therefore, expect isobutane to give two isomeric pentanes, as shown by the following structural formulas:





The first one, dimethyl ethyl methane, is identical with the isopentane obtained from normal butane. The two butanes should yield, then, three distinct monomethyl derivatives. These three compounds have been prepared, and on investigation their formulas have been shown to be as represented. Only three pentanes have ever been discovered. This fact tends to confirm our ideas concerning the structure of the butanes.

An examination of the structural formulas of the three pentanes shows that there are five possible isomeric hexanes which are compounds having the same molecular formula  $\text{C}_6\text{H}_{14}$ , but which are different in their chemical and physical properties. In order to distinguish these substances, they are represented by different structural formulas. Only five hexanes are known, and consequently the theory of structural formulas is in accordance with the experimental facts.

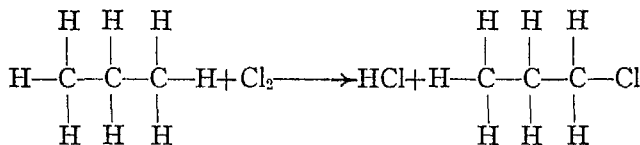
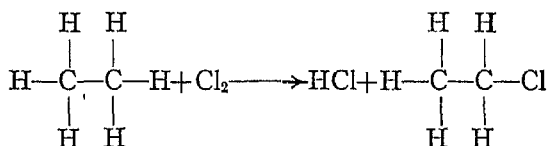
**Open-chain compounds.** Propane,  $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ , is repre-

sented by a structural formula which shows that the carbon atoms are linked together as in a chain. A compound which has this kind of a formula is called an *open-chain compound*. The carbon atoms in the structural formula of propane are represented as being joined together by a single link, or bond, and conse-



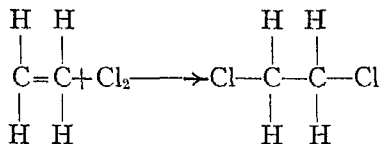
quently compounds such as propane, propyl chloride, and normal butane are frequently called *single-bond compounds*. The term "single bond" means, then, the single link connecting any two carbon atoms. It represents a condition which is supposed to exist between the carbon atoms of saturated hydrocarbons and their derivatives.

The principal characteristic of these single-bond, saturated compounds is that they react only by substitution, as shown by the following equations:



In this respect they differ from the unsaturated double-bond

compounds, such as ethylene  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ , which react only by addition:



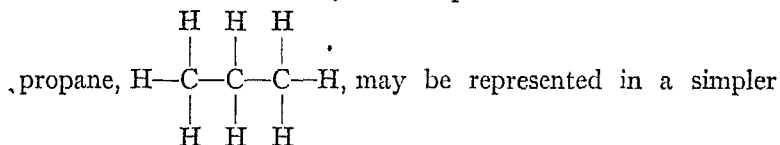
The unsaturated compounds will be considered in the next chapter.

There are a larger number of compounds of carbon than of any other element. This is due to the fact that carbon atoms have the ability to unite with each other to form carbon chains.

## COMPLETE AND ABBREVIATED STRUCTURAL FORMULAS

NAME OF COMPOUND	COMPLETE STRUCTURAL FORMULA	ABBREVIATED STRUCTURAL FORMULA
Methane	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	$\text{CH}_4$
Methyl chloride	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{Cl} \\   \\ \text{H} \end{array}$	$\text{CH}_3\text{Cl}$
Ethane	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_3$
Ethyl bromide	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{Br} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{Br}$ or $\text{C}_2\text{H}_5\text{Br}$
Propane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_3$
Propyl chloride (normal)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Cl} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
Propyl chloride (iso)	$\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 > \text{CHCl} \end{array}$ or $(\text{CH}_3)_2\text{CHCl}$
Butane (normal)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
Butane (iso)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{C} \quad \text{H} \\   \\ \text{H} \end{array}$	$\text{CH}(\text{CH}_3)_3$

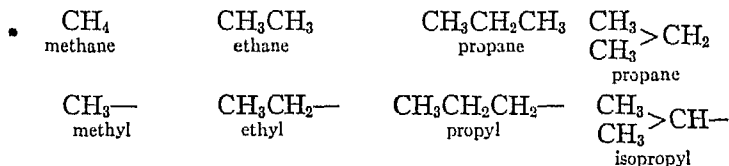
**Abbreviated structural formulas.** As it requires considerable space to write the complete structural formula of an organic compound, it is usually more convenient to write an abbreviated structural formula. Thus, the complete structural formula of



manner by the abbreviated structural formula  $\text{CH}_3\text{CH}_2\text{CH}_3$ . In order to understand the abbreviated structural formula of a compound, one should be familiar with the complete structural formula of that substance. The complete and the abbreviated structural formulas of a few of the compounds we have studied are given on page 46.

**Alkyl radicals.** As we have already explained, a radical is a group of atoms which passes unchanged from one compound to another. We have studied a number of compounds containing different radicals. Thus methyl chloride,  $\text{CH}_3\text{Cl}$ , contains the methyl radical ( $\text{CH}_3$ ); ethyl bromide,  $\text{C}_2\text{H}_5\text{Br}$ , contains the ethyl radical ( $\text{C}_2\text{H}_5$ ) or ( $\text{CH}_3\text{CH}_2$ ); propyl chloride,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ , contains the propyl radical ( $\text{CH}_3\text{CH}_2\text{CH}_2$ ) and isopropyl chloride,  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 > \text{CH} \end{array} \text{Cl}$ , contains the isopropyl radical  $[(\text{CH}_3)_2\text{CH}]$ . Dimethyl ethyl methane,  $(\text{CH}_3)_2\text{CHC}_2\text{H}_5$ , contains two methyl radicals and one ethyl radical. Radicals such as methyl, ethyl, propyl, and isopropyl are called *alkyl radicals*.

Theoretically an alkyl radical is considered as derived from a molecule of a paraffin hydrocarbon by the removal of one hydrogen atom:



Thus, as shown by the formulas above, the methyl radical is derived from methane, ethyl from ethane, propyl and isopropyl from propane.

**Paraffin hydrocarbons.** The paraffin hydrocarbons are single-bond, saturated compounds. They do not combine directly with other elements and react only by substitution. The following table gives the molecular formulas, abbreviated structural formulas, and boiling points of the simple paraffins and simple isomers of this homologous series of hydrocarbons:

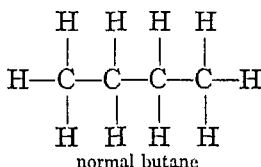
PARAFFIN HYDROCARBONS

MOLECULAR FORMULA	NAME	ABBREVIATED STRUCTURAL FORMULA	BOILING POINT, °C.
$\text{CH}_4$	Methane	$\text{CH}_4$	-164
$\text{C}_2\text{H}_6$	Ethane	$\text{CH}_3\text{CH}_3$	-93
$\text{C}_3\text{H}_8$	Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	-45
$\text{C}_4\text{H}_{10}$	Butane (normal)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	1
	Butane (iso)	$\text{CH}(\text{CH}_3)_3$	-17
$\text{C}_5\text{H}_{12}$	Pentane (normal)	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	36.4
	Dimethyl ethyl methane	$(\text{CH}_3)_2\text{CHC}_2\text{H}_5$	30.4
	Tetramethyl methane	$\text{C}(\text{CH}_3)_4$	9

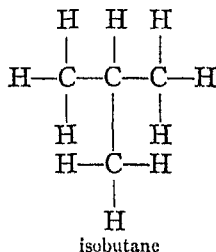
As shown by the preceding table, there are one methane, one ethane, and one propane. There are two paraffin hydrocarbons having the molecular formula  $\text{C}_4\text{H}_{10}$ . They are normal butane and isobutane. These isomers are distinguished by representing them by different structural formulas. Three paraffin

hydrocarbons have the molecular formula  $C_6H_{12}$ . They are normal pentane, dimethyl ethyl methane, and tetramethyl methane. Like the isomeric butanes these isomers are also distinguished by different structural formulas.

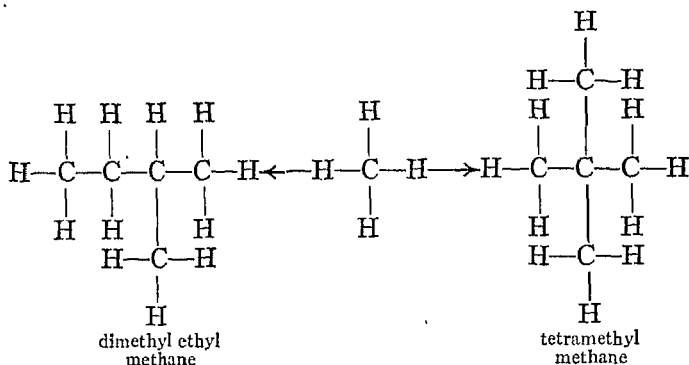
There are two general kinds of paraffin hydrocarbons which are known as normal and iso compounds. In the normal paraffins the carbon atoms are connected in a continuous chain, as shown by the formula of normal butane:



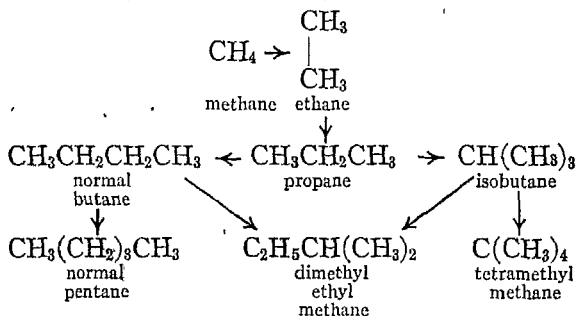
In these normal compounds no carbon atom is directly combined with more than two others. In the iso compounds all the carbon atoms are not connected in a continuous chain because the compound contains a side chain, as shown by the formula of isobutane:



In naming the iso paraffins they are regarded as substituted methanes. The carbon atom which is united to the largest number of other carbon atoms is considered as the carbon of the original methane from which they are derived. Thus two of the pentanes are regarded as derivatives of methane:



**Derivation of the paraffin hydrocarbons.** As previously stated, all the hydrogen atoms in methane have equal value; and methane, as shown by the outline below, yields only one methyl derivative, which is methyl methane or ethane:



The student should learn to distinguish between the terms "derivation" and "preparation." Ethane is the methyl derivative of methane, but it is not prepared from methane. It is prepared from methyl chloride or methyl iodide by treating either of these compounds with sodium. All the hydrogen atoms in ethane have equal value, and ethane therefore yields only one methyl derivative, which is propane. How is propane prepared? Propane contains two different sets of hydrogen atoms which are not united to the molecule in the same manner, and yields two isomeric monomethyl derivatives, which are normal butane

and isobutane. Normal butane yields two isomeric methyl derivatives, which are normal pentane and dimethyl ethyl methane. Isobutane yields the methyl derivative tetramethyl methane and another methyl derivative, dimethyl ethyl methane, which is also derived from normal butane. These compounds may also be considered as derived from methane and are named accordingly.

**Petroleum.** As previously stated, many of the paraffin hydrocarbons are obtained from petroleum. Petroleum is an oil which is obtained from natural springs or artificial borings. It occurs in the United States in Pennsylvania, Ohio, Texas, and other states. It also occurs in Baku, Russia, and other parts of the world. It is used commercially as a source of illuminating oil and of other valuable substances. Pennsylvania petroleum consists mostly of a mixture of paraffin hydrocarbons, while the Russian petroleum consists largely of other hydrocarbons. The crude petroleum is usually distilled and separated into various fractions suitable for particular purposes. When the Pennsylvania petroleum is distilled, it is separated into fractions which, as indicated below, consist of various paraffin hydrocarbons. The fractions thus obtained are known commercially by certain names, such as petroleum ether, kerosene, etc.

These various fractions are purified by washing with sulfuric acid, which removes basic substances, and with sodium hydroxide, which removes acid substances. Oils from certain districts frequently contain sulfur compounds, which may be removed by distilling the oils in the presence of copper.

The first fraction, known commercially as petroleum ether, is the distillate collected at temperatures ranging from about  $40^{\circ}$  to  $70^{\circ}$ . It is used as a solvent for various organic compounds. Benzine, which is the fraction collected from about  $70^{\circ}$  to  $90^{\circ}$ , is also used as a solvent for various substances. Ligroin ( $90^{\circ}$ – $120^{\circ}$ ) is employed as a solvent for certain oils, resins, and other substances. Gasoline is a mixture of benzine and ligroin.

Kerosene ( $150^{\circ}$ – $300^{\circ}$ ) is an illuminant which is burnt in lamps. The lubricating oils, which are present in the fraction boiling above  $300^{\circ}$ , are used as lubricants for machinery. When distilled in a partial vacuum, these lubricating oils yield vaseline (petrolatum). Paraffin is also obtained from the high-boiling lubricating oils.

#### PETROLEUM DISTILLATES

FRACTIONS		BOILING POINT, $^{\circ}\text{C}$	HYDROCARBONS
Petroleum ether		40–70	pentane $\text{C}_5\text{H}_{12}$ hexane $\text{C}_6\text{H}_{14}$
Gasoline	Benzine	70–90	hexane $\text{C}_6\text{H}_{14}$ heptane $\text{C}_7\text{H}_{16}$
	Ligroin	90–120	heptane $\text{C}_7\text{H}_{16}$ octane $\text{C}_8\text{H}_{18}$
Kerosene		150–300	octane and more complex hydrocarbons
Lubricating oils		above 300	hydrocarbons more complex than those of kerosene

#### HALOGEN DERIVATIVES OF THE PARAFFIN HYDROCARBONS

In discussing the paraffin hydrocarbons a number of the halogen derivatives of the paraffins, such as methyl chloride and ethyl chloride, were mentioned. In the table on the opposite page are given the abbreviated structural formulas and the boiling points of a few of the halogen derivatives of the paraffins.

Many of the alkyl halogen compounds are liquids which have pleasant odors, and are insoluble in water. Most of them are heavier than water. As previously stated, the paraffins react with chlorine and bromine, yielding halogen derivatives. This method of preparation yields mixtures of compounds which are difficult to separate, and consequently the monohalogen derivatives

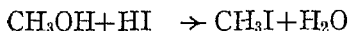
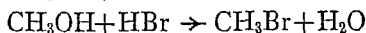
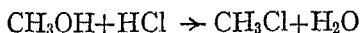


of the paraffins, or alkyl halides, are usually prepared by treating the corresponding alcohols with the proper halogen acids.

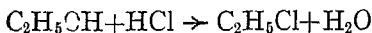
# ALKYL HALOGEN COMPOUNDS

NAME	FORMULA	BOILING POINT, °C.	NAME	FORMULA	BOILING POINT, °C.
Methyl chloride	$\text{CH}_3\text{Cl}$	-24	Ethyl chloride	$\text{C}_2\text{H}_5\text{Cl}$	12.2
Methylene chloride	$\text{CH}_2\text{Cl}_2$	41	Ethyl bromide	$\text{C}_2\text{H}_5\text{Br}$	38.4
Chloroform	$\text{CHCl}_3$	61	Ethyl iodide	$\text{C}_2\text{H}_5\text{I}$	72
Carbon tetra- chloride	$\text{CCl}_4$	76	Propyl chloride (normal)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	46.5
Methyl bromide	$\text{CH}_3\text{Br}$	4.5	Propyl chloride (iso)	$\text{CH}_3\text{CHClCH}_3$	37
Bromoform	$\text{CHBr}_3$	151	Propyl bromide (normal)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	71
Methyl iodide	$\text{CH}_3\text{I}$	45	Propyl bromide (iso)	$\text{CH}_3\text{CHBrCH}_3$	59.5
Methylene iodide	$\text{CH}_2\text{I}_2$	180	Propyl iodide (normal)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	102.5
Iodoform	$\text{CHI}_3$		Propyl iodide (iso)	$\text{CH}_3\text{CHICH}_3$	89.5

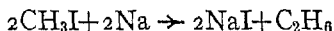
Thus methyl chloride,  $\text{CH}_3\text{Cl}$ , methyl bromide,  $\text{CH}_3\text{Br}$ , and methyl iodide,  $\text{CH}_3\text{I}$ , are obtained from methyl alcohol,  $\text{CH}_3\text{OH}$ , by the following reactions :



In like manner the halogen derivatives of ethane, such as ethyl chloride, may be obtained from ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ ,



The alkyl halides react readily with various substances and are frequently used in preparing organic compounds. They interact with sodium, yielding hydrocarbons,



When treated with water or dilute alkali solutions they are decomposed, yielding alcohols. Thus ethyl alcohol may be obtained by hydrolyzing ethyl bromide or by treating ethyl bromide with an alkali solution (see Experiment 17),



Some of the halogen compounds given in the preceding table are substances of considerable practical importance.

**Chloroform**,  $\text{CHCl}_3$ , is prepared by distilling a mixture of alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , and bleaching powder. The reaction which takes place is rather complex. Chloroform is a liquid which has a pleasant odor and boils at  $61^\circ$ . The vapor of chloroform produces unconsciousness when inhaled, and consequently it is used as an anesthetic in surgery.

**Carbon tetrachloride**,  $\text{CCl}_4$ , is a liquid having a pleasant odor. It is used as a solvent for organic compounds.

**Iodoform**,  $\text{CHI}_3$ , is used medicinally as an antiseptic powder.

**Ethyl chloride**,  $\text{C}_2\text{H}_5\text{Cl}$ , is very volatile and when sprayed upon the surface of the body produces an extremely cold and freezing sensation. It is used as a local anesthetic.

# QUESTIONS

1. What is meant by a homologous series?
2. How is methane prepared?
3. What is a substitution reaction? Give an example.
4. Give two names for each of the following compounds:  $\text{CH}_3\text{Cl}$ ;  $\text{CH}_2\text{Cl}_2$ ;  $\text{CHCl}_3$ .
5. What are saturated compounds?
6. What are outline equations?
7. Carbon tetrachloride may be prepared from methane by a series of reactions. Write these reactions with outline and balanced equations.
8. How are crystalline organic compounds preserved?
9. Write an equation showing the preparation of ethane.
10. Show by equations how hexabrom ethane may be prepared from ethane.
11. Explain, with equations, the laboratory preparation and purification of ethyl bromide.
12. How are liquid organic compounds preserved?
13. What is meant by the theoretical and actual yield?
14. Write an equation showing the preparation of propane.
15. What is meant by synthetic chemistry?
16. Write outline reactions showing the preparation of propane from methane.
17. What are isomeric compounds? Give examples.
18. How are the structural formulas of methane, ethane, and propane determined?
19. Ethyl bromide has no isomer. How does this fact tend to show the relations of the hydrogen atoms in ethane?
20. Propane is represented by a structural formula which shows that the hydrogen atoms are related in two different ways to the carbon atoms. How many monobrom substitution derivatives should propane yield?
21. Write the complete and abbreviated structural formulas of the isomers, propyl chloride and isopropyl chloride.
22. What is meant by a normal compound and an iso compound?
23. Write the complete and abbreviated structural formulas of the monomethyl derivatives of propane and of the isomeric butanes.
24. Propane is the methyl derivative of ethane. Is it prepared from ethane?
25. What is meant by the "derivation" and "preparation" of compounds?
26. What are alkyl radicals? Give examples.
27. How are monohalogen derivatives of the paraffins, such as  $\text{CH}_3\text{Cl}$  and  $\text{C}_2\text{H}_5\text{Cl}$ , usually prepared? What products are obtained when they are hydrolyzed?
28. For what purposes are chloroform, iodoform, and ethyl chloride used?
29.  $\text{C}_2\text{H}_5\text{OH} + \text{HI} \rightarrow \text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O}$ .  
In preparing ethyl iodide from ethyl alcohol according to the equation above, a student obtained 17.5 grams of ethyl iodide from 23 grams of ethyl alcohol.  
Calculate the percentage yield and percentage loss.
30. What important commercial products are obtained by distilling petroleum?

## CHAPTER THREE

### UNSATURATED HYDROCARBONS

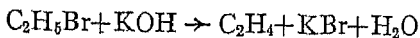
THE second series of aliphatic hydrocarbons is called the *olefines*. The name "olefine" refers to "oil making," because it was found that the first member of this series forms an oil when treated with chlorine. A few of the simpler members of this series are given in the following table :

OLEFINE SERIES OF HYDROCARBONS

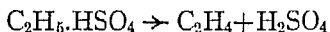
NAME	FORMULA	BOILING POINT, °C.	PHYSICAL STATE
Ethylene . . . . .	$C_2H_4$	-103	Gas
Propylene . . . . .	$C_3H_6$	-48.5	Gas
Butylene . . . . .	$C_4H_8$	-5	Gas
Amylene . . . . .	$C_5H_{10}$	35	Liquid

These hydrocarbons form a homologous series containing two atoms of hydrogen less than the corresponding paraffin hydrocarbons which have the same number of carbon atoms. Thus ethane, which has two carbon atoms, has the formula  $C_2H_6$ , while ethylene, which also has two carbon atoms, has the formula  $C_2H_4$ . What is meant by "a homologous series"? The simplest member corresponding to methane would be methylene,  $CH_2$ ; a compound having this formula is unknown, and all attempts to prepare it have been unsuccessful.

**Ethylene**,  $C_2H_4$ , which is the first member of this series, is a colorless gas and burns with a luminous flame. It occurs in coal gas, the luminosity of which is due to a certain extent to the presence of ethylene. It may be prepared in several ways, one of which is by treating ethyl bromide with a hot alcoholic solution of potassium hydroxide,

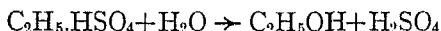


How would ethyl bromide react when treated with a dilute aqueous solution of potassium hydroxide? The usual laboratory method used in preparing ethylene consists in treating ethyl alcohol, which has the formula,  $C_2H_5OH$ , with sulfuric acid:



Ethyl alcohol may be regarded as ethane in which one hydrogen atom is replaced by the hydroxyl group (OH). At  $100^\circ$  it reacts with the sulfuric acid, forming the compound ethyl hydrogen sulfate,  $C_2H_5.HSO_4$ , and water. The water formed in this reaction is taken up by the excess sulfuric acid, which acts as a dehydrating agent. At higher temperatures,  $170^\circ$ , the ethyl hydrogen sulfate decomposes, giving ethylene. The reaction takes place in two stages. By mixing the materials in appropriate proportions and heating to the proper temperature it is possible to separate out the intermediate product, ethyl hydrogen sulfate. Ethyl hydrogen sulfate may be regarded as sulfuric acid in which one of the hydrogen atoms has been replaced by the ethyl radical. It is similar in structure to sodium hydrogen sulfate,  $NaHSO_4$ .

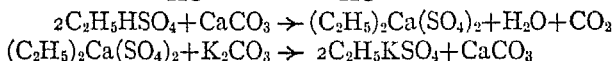
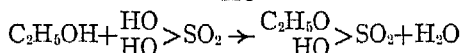
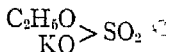
Ethyl hydrogen sulfate, when boiled with water, decomposes into ethyl alcohol and sulfuric acid,



It is easily converted into ethyl potassium sulfate,  $C_2H_5KSO_4$ , which is a more stable compound.

## EXPERIMENT 12

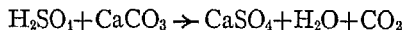
### Preparation of ethyl potassium sulfate



<i>Materials</i>	{ 43 cc. absolute alcohol
	{ 14 cc. concentrated sulfuric acid
	{ Calcium carbonate
	{ 25 grams potassium carbonate

*Procedure.* Pour 43 cc. of absolute alcohol into a 300 cc. round flask. To this add, with constant shaking and cooling, 14 cc. of concentrated sulfuric acid. The flask is now

connected to a reflux condenser as shown in Figure 8, placed upon a water bath, and heated about 2 hours. The materials in the flask are protected from atmospheric moisture by connecting the top of the condenser with a calcium chloride tube *D*, filled with granulated calcium chloride. The tube should be filled in the same manner as the chloride tube in Experiment 6. The reaction product consists of ethyl hydrogen sulfate together with some free sulfuric acid and unchanged alcohol. The apparatus is disconnected and the product is poured into about 300 cc. of water contained in a 500 cc. evaporating dish. Powdered calcium carbonate is now added until the liquid is neutral. This changes the ethyl hydrogen sulfate into the neutral, ethyl calcium sulfate,  $(C_2H_5)_2Ca(SO_4)_2$ , and neutralizes the excess of sulfuric acid:



The mixture is filtered through a cloth (muslin) filter, after which it is refiltered through ordinary coarse filter paper. The clear solution is now warmed on a water bath, and to it is added a solution con-

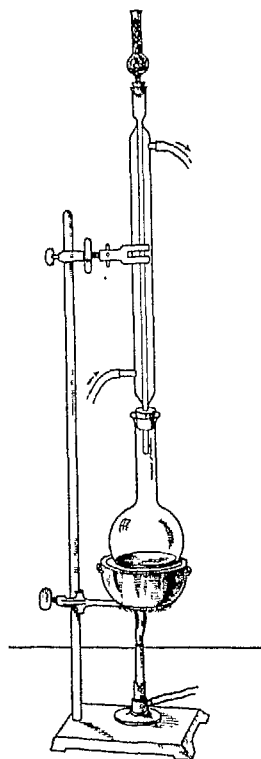


Figure 8

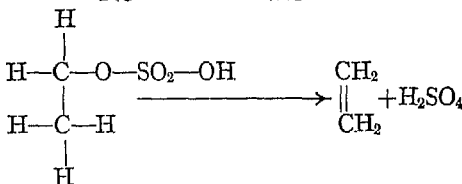
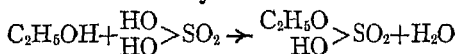
taining 25 grams of potassium carbonate until all the calcium is precipitated as carbonate and the liquid is slightly alkaline. To determine when a sufficient amount of potassium carbonate has been added, filter about 20 cc. of the liquid, add to it a few drops of potassium carbonate solution, and observe if a further precipitation of

calcium carbonate is obtained. The carbonate solution converts the calcium salt,  $(\text{C}_2\text{H}_5)_2\text{Ca}(\text{SO}_4)_2$ , into the soluble potassium salt,  $\text{C}_2\text{H}_5\text{KSO}_4$ . The mixture is filtered as before, poured into an evaporating dish, placed on a water bath, and evaporated until the salt begins to crystallize out on the side of the dish. The dish is now set aside and the salt allowed to crystallize, after which it is filtered and dried on filter paper. Weigh the amount obtained and calculate the percentage yield. Preserve a specimen in a sealed tube.

Ethylene is obtained by heating a mixture of ethyl alcohol and sulfuric acid in the proper proportions at a temperature of  $170^\circ$ . The intermediate product, ethyl hydrogen sulfate, which is formed at about  $100^\circ$ , is decomposed at  $170^\circ$ , yielding ethylene.

## EXPERIMENT 13

Preparation of ethylene,  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array}$ , and behavior of unsaturated hydrocarbons



*Materials*  $\left\{ \begin{array}{l} 30 \text{ cc. absolute ethyl alcohol} \\ 80 \text{ cc. concentrated sulfuric acid} \\ \text{Concentrated solution of sodium hydroxide} \end{array} \right.$

*Procedure.* Pour 30 cc. of absolute ethyl alcohol into a liter round distilling flask. Gradually add to this, in small portions and with constant shaking and cooling, 80 cc. of concentrated sulfuric acid. After the materials have been mixed and cooled, the apparatus should be connected as shown in Figure 9. The liter flask *A* contains the mixture of acid and alcohol. It is fitted with a one-hole rubber stopper through which passes a thermometer. The thermometer is so adjusted that the mercury bulb dips just below the surface of the mixture in the

flask. The gas wash bottle *B* contains a small amount of concentrated sulfuric acid, while *C* is a wash bottle containing a concentrated

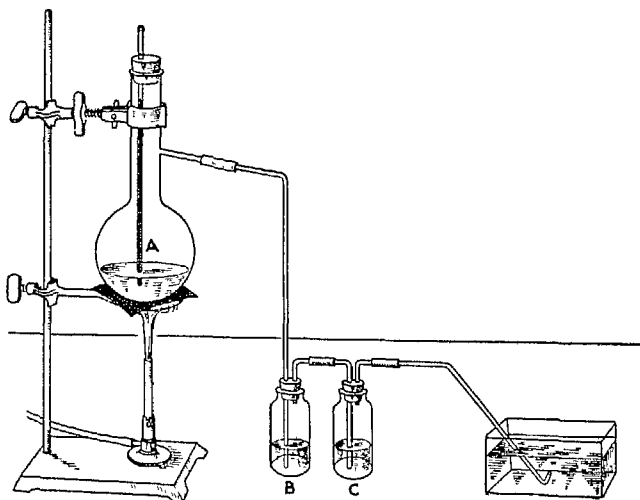


Figure 9

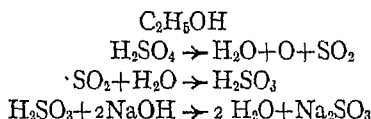
solution of sodium hydroxide. The surface of the solution in each of the wash bottles should not be more than about 0.5 cm. above the lower end of the tube which dips into the solution. The exit end of bottle *C* is connected to a rubber tube which dips into a pneumatic trough containing water.

When ordinary salt bottles are used as gas wash bottles the stoppers frequently leak. It is better to use the usual Drechsel wash bottles which have ground-glass stoppers. When the Drechsel bottles are used, the stoppers should be greased with burette grease to prevent them from "sticking."

See that the apparatus is arranged properly according to the diagram and that all connections are tight. The flask *A* is heated gradually over a wire gauze until the thermometer shows a temperature of  $170^{\circ}$ . The flask should be heated steadily so that a constant stream of gas is obtained. If the reaction mixture foams with the separation of black carbonaceous matter, disconnect flask *A* from the wash bottle *B* and allow to cool. Then connect the apparatus, and start the experiment, once more, or empty the flask *A* and renew the mixture.

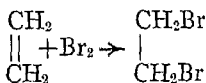


The gas generated by the mixture should pass through the solutions in the bottles *B* and *C* and be collected by displacement in inverted test tubes filled with water and held by the hand in the pneumatic trough. At 170° sulfuric acid and ethyl alcohol react to form ethylene. The gas contains impurities and, in order to purify it, is passed through the wash solutions. The impurities are alcohol, ether, and sulfur dioxide. A portion of the alcohol in the reaction mixture distills over with the ethylene and is absorbed by the sulfuric acid. As a result of side reactions, a small amount of ether is formed (see preparation of ether). A portion of the alcohol reduces the sulfuric acid, forming sulfur dioxide, and this is absorbed by the alkali solution:



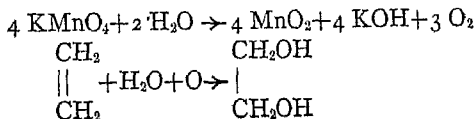
*A.* Collect a test tube full of the gas and apply a lighted match. Does it burn?

*B.* Fill two test tubes with the gas and close them securely with stoppers. Open one of the tubes and add 0.5 cc. of pale-yellow, dilute bromine water. Close the bottle immediately with a stopper, and shake. The bromine solution is decolorized rapidly. The double-bond compound ethylene reacts with the bromine by addition, giving the colorless ethylene dibromide (dibrom ethane),



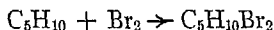
Notice that no hydrogen bromide is formed in this reaction and consequently the action is one of addition and not substitution.

*C.* Into the second bottle containing the gas pour 0.5 cc. of a dilute rose-colored potassium permanganate solution; add 1 cc. of potassium carbonate solution (1 : 10). Close the bottle again, and shake. Notice that the permanganate solution also is immediately decolorized:

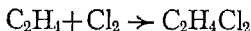


The alkaline permanganate solution is reduced and the ethylene is oxidized to ethylene glycoll,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , which is a dihydroxy derivative of ethane.

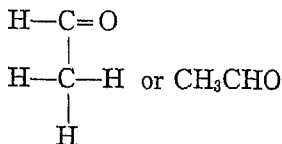
D. Other unsaturated, double-bond compounds behave in a manner similar to ethylene. To 5 cc. of amylene,  $\text{C}_5\text{H}_{10}$ , add 5 cc. of a solution consisting of 4 cc. of bromine dissolved in 100 cc. of carbon tetrachloride. (The stock room supplies this solution.) Notice that the bromine solution is decolorized immediately. The amylene is converted to amylene dibromide,  $\text{C}_5\text{H}_{10}\text{Br}_2$ :



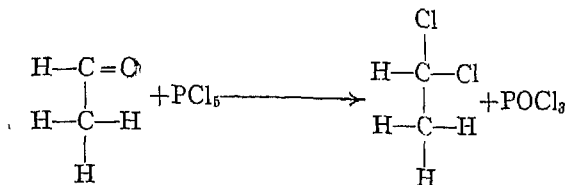
When ethylene is treated with chlorine, it reacts by addition, taking up two atoms of chlorine,



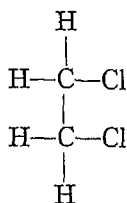
The compound  $\text{C}_2\text{H}_4\text{Cl}_2$  may be regarded as an addition product of ethylene and is called *ethylene dichloride*. It may also be looked upon as ethane in which two hydrogen atoms have been substituted by two atoms of chlorine. It may be regarded as a dichlor substitution product of ethane and consequently is called *dichlor ethane*. Ethylene dichloride is a colorless liquid boiling at  $85^\circ$ . It furnishes an interesting example of an isomeric compound, as there are two isomeric dichlor ethanes which have the molecular formula  $\text{C}_2\text{H}_4\text{Cl}_2$ , but different physical and chemical properties. One of these, ethylidene chloride, is obtained from acetaldehyde. Acetaldehyde has the formula,



and when this substance is treated with phosphorus pentachloride, the one atom of oxygen is substituted by two univalent atoms of chlorine, as shown by the following equation :

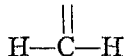


In ethylidene chloride,  $\text{CH}_3\text{CHCl}_2$ , we have, then, two atoms of chlorine united to one carbon atom. Since this compound is isomeric with ethylene dichloride, we must represent the latter by a different structural formula. There is only one other way in which we could write the formula of ethylene dichloride so that it would be distinctly different from that of ethylidene chloride, and that is as



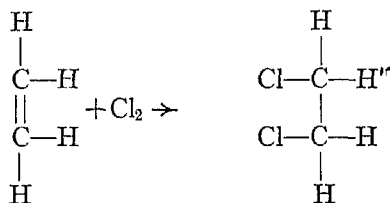
where the two chlorine atoms are united to different carbon atoms. As this formula is in harmony with the general behavior of this compound, it is accepted as the most appropriate formula of ethylene dichloride.

**Structure of ethylene.** The constitutional formula  $\text{H}-\text{C}-\text{H}$

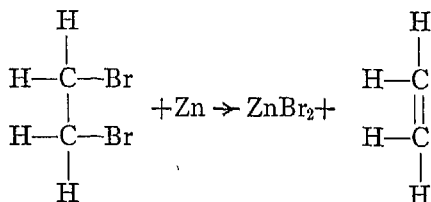


or  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array}$  has been found to represent in a satisfactory manner the

chemical behavior of ethylene. We know that ethylene is an unsaturated compound and reacts by addition, taking up two atoms of some univalent element like chlorine,



As we have already shown, it seems highly probable that in ethylene dichloride the two chlorine atoms are united to different carbon atoms. As this compound is formed by the interaction of ethylene and chlorine, it appears most likely that ethylene consists simply of two methylene groups ( $\text{CH}_2$ ) united together, and when ethylene reacts with chlorine each methylene radical absorbs one atom of chlorine, as shown by the equation above. Ethylene may be prepared by passing the vapors of ethylene dibromide over zinc dust:



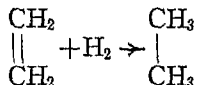
Ethylene dibromide has a structure similar to ethylene dichloride, — that is, the two halogen atoms are united to different carbon atoms, — and when this compound reacts with bromine, the bromine atoms are taken up by the zinc, leaving the two methylene groups, which then unite. This, then, is additional experimental evidence which tends to show that the structural formula of ethylene is written in accordance with its chemical behavior.

**Double bonds.** The manner in which the formula of ethylene is written shows that the carbon atoms are joined by a double bond. A double bond indicates an unsaturated condition, and a compound which has a double bond has the ability to react by

addition, taking up atoms of other elements without giving off any of its own atoms. It is customary to represent the combining capacity of an atom as distributed uniformly in the molecule. The double-bond formula of ethylene shows that each carbon atom is tetravalent, but that its combining capacity is not fully utilized. It indicates that the molecule has an accumulation of combining capacity and that each carbon atom still has the ability to unite with a monovalent atom. We do not know the exact relation existing between the carbon atoms in ethylene, but we do know that the chemical behavior of ethylene is quite different from that of ethane, which is a saturated compound and can react only by substitution. This difference in chemical behavior is represented by single and double bonds:



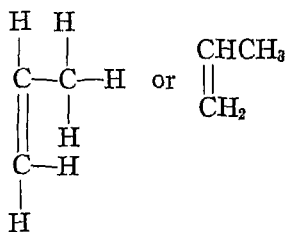
Ethylene reacts with hydrogen, forming the compound ethane,



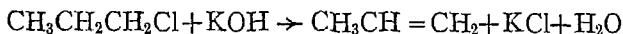
In a reaction of this kind, where a double-bond unsaturated compound enters into direct combination, forming a single-bond saturated compound, the double bond is said to be broken. Double-bond compounds always combine with an even number of monovalent atoms or groups, because they always contain an even number of unsaturated carbon atoms.

•Propylene,  $\begin{array}{c} \text{CHCH}_3 \\ || \\ \text{CH}_2 \end{array}$ , the second member of the olefine hydro-

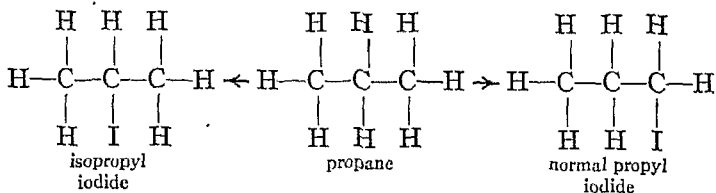
carbons, is a gas. The data obtained from laboratory experiments show that the structural formula of propylene is



It may be regarded as ethylene in which one hydrogen atom has been replaced by the methyl radical, and hence it is methyl ethylene. Just as ethylene may be prepared by the interaction of ethyl bromide and an alcoholic solution of potassium hydroxide, in a similar manner propylene is obtained by heating propyl chloride with an alcoholic solution of potassium hydroxide:

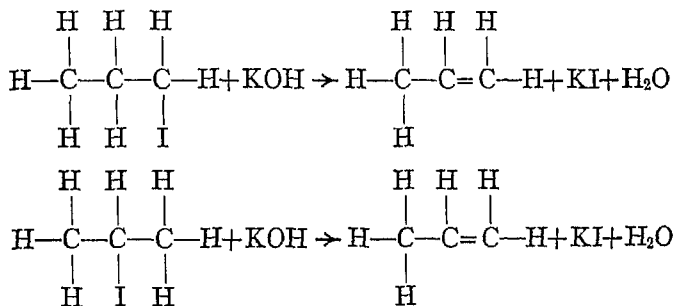


It is also prepared from either of the isomeric propyl iodides. Two isomeric moniodo derivatives of propane having structures similar to the propyl chlorides are known. They are normal propyl iodide,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ , and isopropyl iodide,  $\text{CH}_3\text{CHICH}_3$ . Normal propyl iodide is regarded as propane in which an atom of hydrogen in one of the end methyl groups has been substituted by an atom of iodine, and isopropyl iodide is considered as propane in which an atom of hydrogen in the methylene group has been replaced by an atom of iodine:

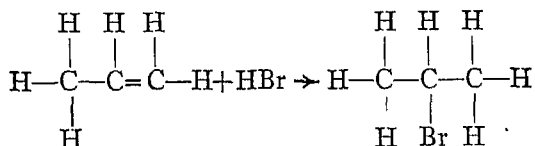


Either of these iodides reacts with an alcoholic solution of potassium hydroxide, giving off an atom of hydrogen and an atom of iodine, forming propylene. It is, therefore, evident that in the formation of propylene from propyl iodide, or isopropyl iodide,

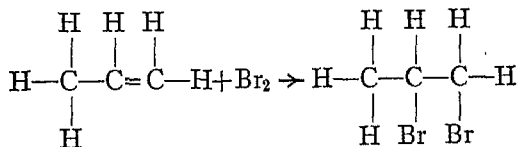
the atom of hydrogen and the atom of iodine which are given off must be united to different carbon atoms and not to the same one, and consequently the reactions take place as shown by the following equations:



Propylene is, therefore, represented by a formula containing a double bond, which shows that it is an unsaturated compound. The double-bond formula of propylene is in harmony with its chemical behavior. It unites, by addition, with hydrogen bromide, forming isopropyl bromide:



It also reacts with bromine, forming propylene dibromide:



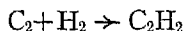
Give another name for propylene dibromide.

The higher members of the olefine series are obtained by methods similar to those employed in the preparation of ethylene. They give reactions characteristic of double-bond, unsaturated compounds.

**Behavior of the olefines.** The olefines are readily acted upon by chlorine or bromine, forming addition products which are saturated compounds and which may be regarded as disubstitution products of the paraffins. They are easily oxidized by chromic acid or by potassium permanganate.

**Triple-bond compounds.** The third series of aliphatic hydrocarbons is known as the *acetylene series*. The first member is called *acetylene*,  $C_2H_2$ , and the second *allylene*,  $C_3H_4$ . Both of these substances are gases. The members of this series contain two hydrogen atoms less than the corresponding members of the olefine series.

**Acetylene**,  $C_2H_2$ , may be prepared by passing hydrogen over carbon heated to the temperature of the electric arc,

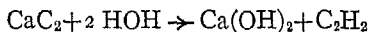


It is easily made in the laboratory from calcium carbide,  $CaC_2$ , which is a substance prepared by heating a mixture of calcium oxide and coke at a very high temperature in an electric furnace.



#### EXPERIMENT 14

**Preparation of acetylene,**  $\begin{array}{c} CH \\ ||| \\ CH \end{array}$



*Materials*  $\left\{ \begin{array}{l} 15 \text{ grams calcium carbide} \\ \text{Water} \end{array} \right.$

**Procedure.** Arrange an apparatus as shown in Figure 10. *A* is a 500 cc. distilling flask containing 15 grams of calcium carbide. The flask is fitted with a stopper which holds a dropping funnel containing water. *B* is an empty flask, and *C*, a pneumatic trough. The object of placing the empty flask between the flask *A* and the trough *C* is to prevent the water in the trough from being drawn back into the flask, thereby causing a violent evolution of gas.

Allow the water in the dropping funnel to drop slowly upon the carbide.



A. Collect a sample of the gas under a test tube of water in the trough and ignite it. Does it burn?

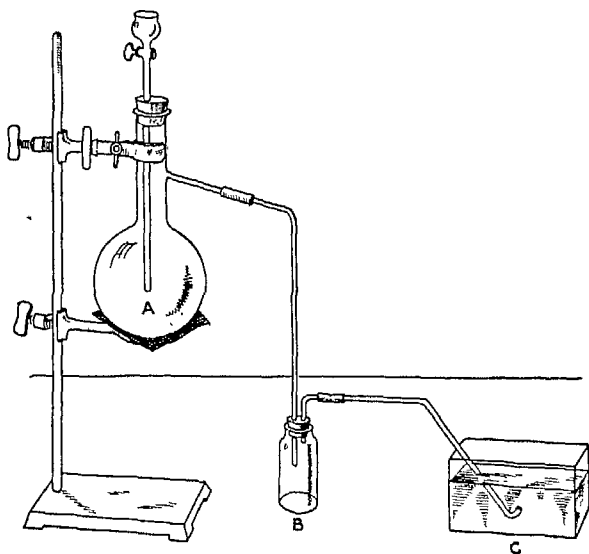
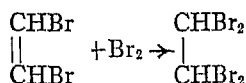
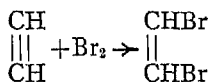


Figure 10

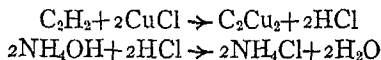
B. Fill a bottle with the gas and add to it about 0.5 cc. of pale-yellow, dilute bromine water. The bottle should be firmly stoppered and shaken a few minutes. Notice that the bromine solution is decolorized,



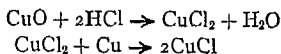
The acetylene reacts by addition, giving the dibromide,  $\begin{array}{c} \text{CHBr} \\ || \\ \text{CHBr} \end{array}$ , and

finally the tetrabromide,  $\begin{array}{c} \text{CHBr}_2 \\ | \\ \text{CHBr}_2 \end{array}$ , of acetylene. Give another name for each of these compounds.

C. Pass acetylene into about 5 cc. of an ammoniacal solution of cuprous chloride. (The stock room supplies this solution.) A brownish-red precipitate of copper acetylide,  $C_2Cu_2$ , is obtained. Filter off the precipitate, and heat about 0.2 gram on a spatula. Notice that it has a tendency to be explosive. The precipitation of an ammoniacal solution of cuprous chloride serves as a delicate test for acetylene and enables us to separate it from other gases:



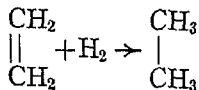
NOTE. The cuprous chloride solution is prepared by dissolving 5 grams of powdered cupric oxide in about 20 cc. of concentrated hydrogen chloride. Add to this solution 5 grams of copper turnings and boil until the green color of the solution changes to dark brown. Then pour it into about 200 cc. of water. A white precipitate of cuprous chloride,  $CuCl$ , is obtained. Allow the precipitate to settle. Decant off the supernatant acid solution and dissolve the precipitate in a solution of ammonia and ammonium chloride, which is prepared by dissolving 20 grams of powdered ammonium chloride in 40 cc. of water and adding 30 cc. of concentrated ammonium. The solution should be poured into a bottle and kept firmly stoppered:



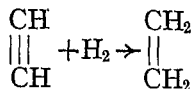
When acetylene is ignited from an ordinary gas burner, it burns with a very smoky flame. However, when especially constructed burners are employed, it gives a very brilliant flame and consequently it is used as an illuminant.

*Structure.* Acetylene is an unsaturated compound and bears the same relation to ethylene as the latter does to ethane. The structural formula which has been assigned to acetylene is  $\begin{smallmatrix} CH \\ ||| \\ CH \end{smallmatrix}$ , and this formula is in harmony with its general chemical

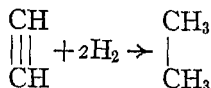
behavior. It represents acetylene as being a *triple-bond* compound, which means that it has a degree of unsaturation greater than a double-bond compound like ethylene. Ethylene reacts with two atoms of hydrogen, forming ethane,



while acetylene reacts with two atoms of hydrogen, forming ethylene,

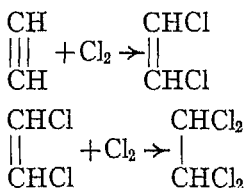


or with four atoms of hydrogen, forming ethane,



Thus by treating acetylene with hydrogen we can break the triple bond and pass to a double-bond compound less unsaturated than acetylene or to a single-bond, saturated compound.

In similar manner acetylene shows its unsaturated condition by reacting with chlorine or bromine, giving addition products:



The compound  $\begin{array}{c} \text{CHCl} \\ || \\ \text{CHCl} \end{array}$  may be regarded as an addition prod-

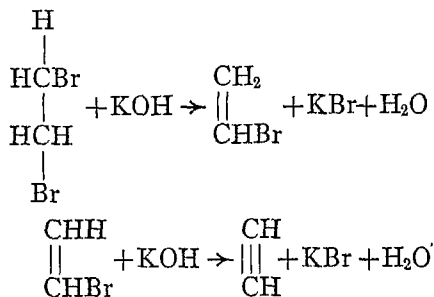
uct of acetylene and hence is called acetylene dichloride. Again, it may be looked upon as a dichlor substitution product of ethylene and therefore may be called *dichlor ethylene*. The compound  $\text{CHCl}_2$

$\begin{array}{c} | \\ \text{CHCl}_2 \end{array}$  also has two names. What are they? Write equations

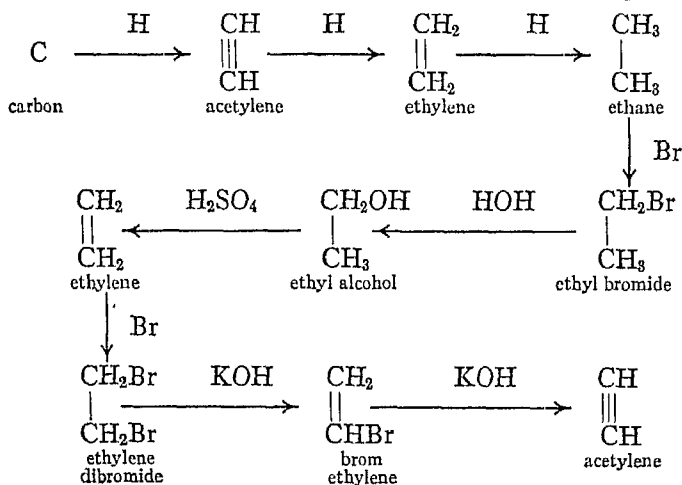
showing the action of bromine on acetylene and name the compounds formed.

Acetylene may be prepared by treating ethylene dibromide with an alcoholic solution of potassium hydroxide. In this experiment the reaction takes place in two stages, and vinyl bromide is formed as an intermediate product. This substance

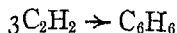
has the formula  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CHBr} \end{array}$  and is therefore monobrom ethylene. The chemistry of this experiment is easily understood, if we assume that acetylene has the structure which has been assigned to it :



These reactions are interesting, as they show how it is possible to prepare, from a single-bond compound, a double- and a triple-bond compound. Thus, starting with the elements carbon and hydrogen, we can prepare by a series of reactions a triple-bond compound and from this pass to a single bond and return again to a triple bond, as shown by the following outline equations :



**Polymeric compounds.** When acetylene gas is passed through a tube heated to dull redness, the compound benzene,  $C_6H_6$ , is formed:



In this reaction the molecule of acetylene is said to *polymerize*, and the compound which is formed is called a *polymer* of acetylene. Acetylene and benzene are, then, polymeric compounds. Polymeric compounds are those which have the same percentage composition but different molecular weights. Calculate the percentage of carbon and hydrogen in acetylene and in benzene.

**Allylene**, the second member of the acetylene series, has the formula  $\begin{array}{c} C-CH_3 \\ ||| \\ CH \end{array}$  and hence it is methyl acetylene. It may be

prepared by the interaction of propylene dibromide and a solution of alcoholic potassium hydroxide:



It is a gas similar to acetylene in its chemical behavior.

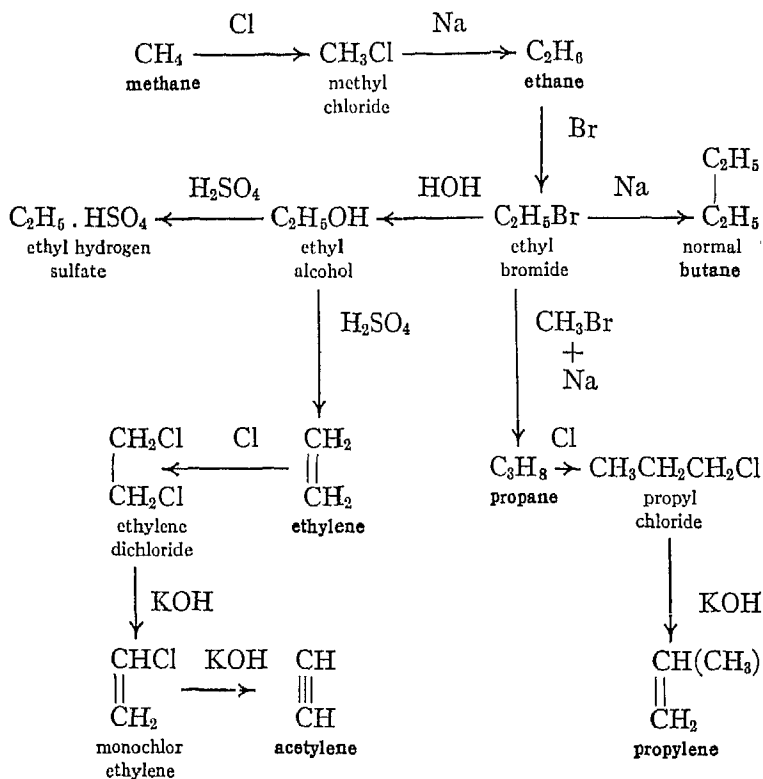
The aliphatic hydrocarbons which we have studied are shown in the following table:

ALIPHATIC HYDROCARBONS

SATURATED COMPOUNDS	UNSATURATED COMPOUNDS	
Paraffins	Olefines	Acetylenes
Methane, $CH_4$ Ethane, $C_2H_6$ Propane, $C_3H_8$ Butanes, $C_4H_{10}$ Pentanes, $C_5H_{12}$	Ethylene, $C_2H_4$ Propylene, $C_3H_6$	Acetylene, $C_2H_2$ Allylene, $C_3H_4$

The synthetic relations between the principal members of these various series of aliphatic hydrocarbons are shown by the following outline equations:

## ALIPHATIC HYDROCARBONS



## QUESTIONS

1. Explain, with equations, the laboratory preparation of ethyl potassium sulfate and ethylene.
2. How do you test for ethylene?
3. How is the structural formula of ethylene determined?
4. Explain, with equations, how the double-bond formula of ethylene agrees with its chemical behavior.
5. What is meant by single- and double-bond compounds, and how do they react?
6. Write the following series of reactions in outline equations:
  - a. ethyl alcohol  $\rightarrow$  ethylene dichloride.
  - b. ethylene  $\rightarrow$  ethyl bromide  $\rightarrow$  normal butane.
7. Explain the laboratory preparation of acetylene.
8. How would you test for acetylene?
9. For what purpose is acetylene used?
10. What products are formed by treating acetylene with hydrogen, chlorine, or bromine?
11. What is meant by a triple-bond compound?
12. By what series of reactions could you prepare acetylene from ethylene?
13. What are polymeric compounds? Give examples.
14. State the various names you could give to the following compounds:  $C_2H_2Cl_2$ ;  $C_2H_2Cl_4$ ;  $CH_2CHBr$ .
15. By what series of reactions could you prepare acetylene from methane?
16. Write the structural formula of propylene.
17. In preparing ethyl potassium sulfate, why is ethyl calcium sulfate made as an intermediate product?

## CHAPTER FOUR

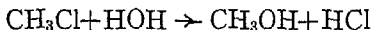
### ALCOHOLS: MONOHYDROXY DERIVATIVES OF THE HYDROCARBONS

WE have studied hydrocarbons, such as methane,  $\text{CH}_4$ , and ethane,  $\text{C}_2\text{H}_6$ , and also halogen derivatives of these hydrocarbons, such as methyl chloride,  $\text{CH}_3\text{Cl}$ , and ethyl chloride,  $\text{C}_2\text{H}_5\text{Cl}$ . The alcohols are hydroxyl (OH) derivatives of the hydrocarbons. These compounds form a homologous series corresponding to the paraffin hydrocarbons:

Methane,  $\text{CH}_4$       Methyl alcohol,  $\text{CH}_4\text{O}$ , or  $\text{CH}_3\text{OH}$

Ethane,  $\text{C}_2\text{H}_6$       Ethyl alcohol,  $\text{C}_2\text{H}_6\text{O}$ , or  $\text{C}_2\text{H}_5\text{OH}$

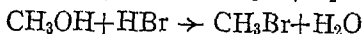
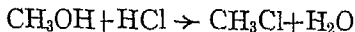
**Methyl alcohol**,  $\text{CH}_3\text{OH}$ , is the simplest alcohol. It may be prepared in various ways, one of which is by the destructive distillation of wood. Consequently it is called *wood alcohol*. By "destructive distillation" is meant that the substance distilled undergoes decomposition into simpler substances which are distilled over and may be separated by redistillation or by other methods. Methyl alcohol may be prepared in the laboratory by the hydrolysis of methyl chloride:



In explaining how a structural formula is determined, we used methyl alcohol as an example and showed that it contained the hydroxyl group united to a methyl group (page 18).

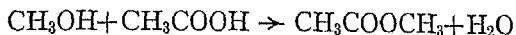
Methyl alcohol is a colorless liquid which boils at  $66^\circ$  and is extensively used as a solvent for organic compounds. It burns with a non-luminous flame which does not deposit soot, and hence is a convenient source of heat. When taken internally it produces intoxication and blindness.

*Reactions.* Methyl alcohol gives reactions which are characteristic of alcohols. When treated with acids, alkyl halides such as methyl chloride or methyl bromide are obtained:

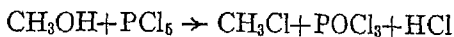




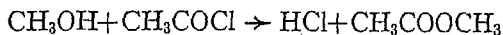
It reacts with acetic acid,  $\text{CH}_3\text{COOH}$ , yielding the methyl ester of acetic acid (methyl acetate),  $\text{CH}_3\text{COOCH}_3$ :



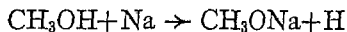
The interaction of methyl alcohol and phosphorus pentachloride yields methyl chloride:



When treated with acetyl chloride,  $\text{CH}_3\text{COCl}$ , methyl acetate and hydrogen chloride are obtained:



When acted upon by sodium, methyl alcohol yields sodium methylate (sodium methoxide),  $\text{CH}_3\text{ONa}$ ,

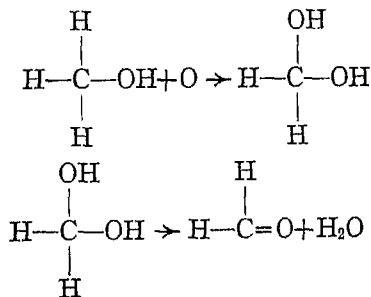


On oxidation, methyl alcohol yields the compound formic aldehyde,

which has the formula  $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}=\text{O} \end{array}$ . In this reaction an un-

stable intermediate product  $\begin{array}{c} \text{OH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$  is probably formed, but

this is decomposed immediately. Experience has shown that one carbon atom cannot hold two hydroxyl groups in combination. When a compound having this structure is formed, it is immediately decomposed and the hydroxyl groups break up, forming water:



The following table contains the formulas of the simpler alcohols and their boiling points. There are also included the halogen derivatives corresponding to these alcohols and the hydrocarbons from which these compounds are derived.

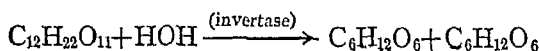
HYDROCARBONS, HALOGEN AND HYDROXYL DERIVATIVES

PARAFFIN HYDROCARBONS	HALOGEN DERIVATIVES	ALCOHOLS	BOILING POINT OF THE ALCOHOLS, °C
CH <sub>4</sub> methane	CH <sub>3</sub> Cl methyl chloride	CH <sub>3</sub> OH methyl alcohol	66
C <sub>2</sub> H <sub>6</sub> ethane	C <sub>2</sub> H <sub>5</sub> Cl ethyl chloride	C <sub>2</sub> H <sub>5</sub> OH ethyl alcohol	78
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl propyl chloride (normal)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH propyl alcohol (normal)	97
	CH <sub>3</sub> CHClCH <sub>3</sub> propyl chloride (iso)	CH <sub>3</sub> CHOHCH <sub>3</sub> propyl alcohol (iso)	82

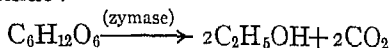
Ethyl alcohol, C<sub>2</sub>H<sub>5</sub>OH, is the second member of this series of alcohols. It is known commercially as *grain alcohol* and is commonly called *alcohol*.

Alcohol may be prepared from cane sugar, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, by means of a microscopic organism called the *yeast plant*. This organism secretes two enzymes known as *invertase* and *zymase*.

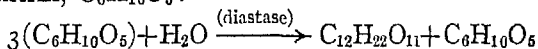
Enzymes are complex organic compounds obtained from plants or animals. They have the ability to act catalytically and accelerate chemical reactions. Cane sugar under the influence of the enzyme invertase is converted into the simpler sugars, glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, and fructose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>:



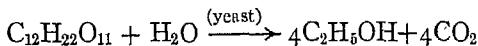
These simpler sugars in the presence of the enzyme *zymase* undergo alcoholic fermentation and are converted into alcohol and carbon dioxide :



Alcohol is usually manufactured from substances which contain starch, such as corn, rye, barley, rice, and potatoes. Malt is a substance prepared by allowing barley to sprout in a moist, warm atmosphere. The enzyme *diastase* occurs in the germinating seeds. When a warm aqueous solution of a substance containing starch,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , is treated with a malt solution which contains *diastase*, the starch under the influence of the enzyme is converted to maltose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , a sugar, and another substance called *dextrin*,  $\text{C}_6\text{H}_{10}\text{O}_5$  :



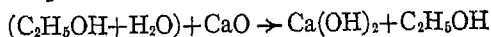
When this change has taken place yeast is added, and as a result the maltose is converted into alcohol and carbon dioxide :



Alcohol as it is ordinarily manufactured contains from 80 to 95 per cent of pure alcohol, together with water and other impurities. By redistillation alcohol having a purity of 95 per cent may be obtained. Absolute alcohol is that which has been distilled over lime. It contains about 0.5 per cent of water. Ethyl alcohol is a colorless liquid which boils at  $78^\circ$  and burns with a non-luminous flame. It is manufactured in large quantities and is used in the preparation of varnishes, perfumes, tinctures, and as a general solvent for organic compounds. When taken internally in sufficient quantities it produces intoxication.

#### EXPERIMENT 15

**Preparation of absolute alcohol,  $\text{C}_2\text{H}_5\text{OH}$**



*Materials* { 250 cc. ethyl alcohol (95 per cent)  
About 100 grams of calcium oxide

As shown by the equation, the water which the alcohol contains is taken up by the lime, forming calcium hydroxide, while the alcohol itself is dehydrated.

*Procedure.* Pour 250 cc. of 95 per cent ethyl alcohol into a dry 1-liter, round flask. Add to this about 100 grams of calcium oxide which has been broken into lumps of approximately 1.5 cm. in diameter. Connect the flask to a dry reflux condenser (see Experiment 12, page 58). A calcium chloride tube containing granulated calcium chloride is now connected to the upper part of the condenser to prevent atmospheric moisture from entering the apparatus.

An actively boiling water bath is placed under the flask, which is heated about 1.5 hours. The flame is now extinguished and the condenser arranged in the usual position for distillation. The end of the condenser is now connected to an adapter, which is fastened securely by means of a cork stopper to a dry filtering flask. The side tube of the filtering flask is connected to a calcium chloride tube containing granulated, anhydrous calcium chloride to prevent the entrance of atmospheric moisture. The arrangement of the apparatus is shown in the following diagram:

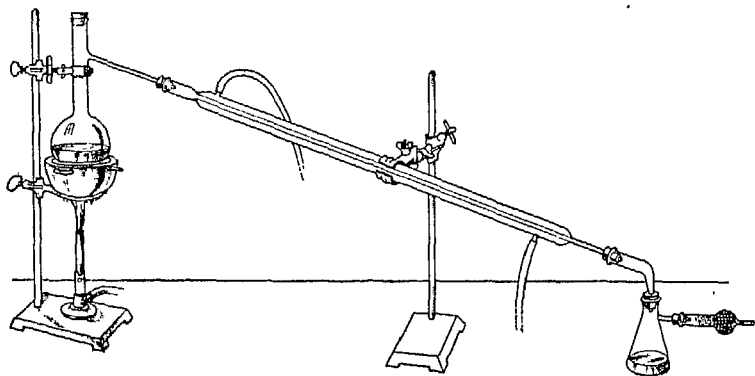
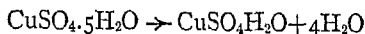


Figure 11

When the entire apparatus has been rearranged, place a boiling water bath under the flask and allow the dehydrated alcohol to distil. When about 15 cc. has distilled over, disconnect the receiver, pour out the distillate, and connect again. The first portion of the distillate usually absorbs moisture from the side of the readjusted apparatus.

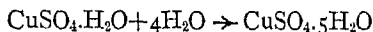
When no more alcohol distils over, extinguish the flame. Pour the contents of the receiver into a dry ground-glass stoppered bottle and keep the bottle securely stoppered.

A. The presence of water in alcohol may be detected by testing with dehydrated copper sulfate. Prepare dehydrated copper sulfate,  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , by heating about 2 grams of crystallized copper sulfate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in a porcelain dish over a wire gauze. Stir the sulfate with a spatula until a faint blue-colored powder is obtained:



The dehydrated copper sulfate prepared in this manner usually consists of a mixture of anhydrous copper sulfate,  $\text{CuSO}_4$ , and the monohydrate,  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ .

Pour 5 cc. of 95 per cent alcohol into a test tube and add to it about 0.5 gram of dehydrated copper sulfate. The dehydrated copper sulfate readily unites with water, forming the deep-blue, hydrated copper sulfate, and thus enables us to test for the presence of water in a sample of alcohol:

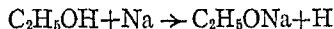


Pour 5 cc. of absolute alcohol into a dry test tube and add 0.5 gram of dehydrated copper sulfate. Is the dehydrated copper sulfate converted into the blue hydrated copper sulfate?

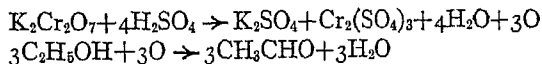
#### EXPERIMENT 16

##### Reactions of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$

A. Pour 5 cc. of absolute alcohol into a test tube, and add a small piece of sodium (0.5 gram). Hydrogen gas is evolved and the alcohol is converted into sodium ethylate,  $\text{C}_2\text{H}_5\text{ONa}$ :



B. Acidify about 3 cc. of potassium dichromate solution (1:10) with about 0.5 cc. of concentrated sulfuric acid and add a few drops of ethyl alcohol. Warm the solution and notice the odor of aldehyde,  $\text{CH}_3\text{CHO}$ :



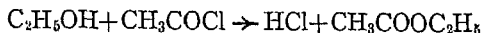
C. Pour 1 cc. of ethyl alcohol into a test tube and add to it a few drops of a dilute sodium hydroxide solution (1:10). Add to the mix-

ture 1 cc. of a potassium iodide solution of iodine. Warm gently and ascertain the odor. Compare with the odor of a specimen of iodoform which you will find in a bottle on the side shelf. Allow the test tube containing the mixture to stand a few minutes, and notice the fine, yellow precipitate of iodoform,  $\text{CHI}_3$ , which precipitates gradually. This is known as the iodoform test for ethyl alcohol:



NOTE. The potassium iodide solution of iodine is prepared by dissolving 5 grams of powdered potassium iodide in 15 cc. of water and adding slowly to this solution 1 gram of powdered iodine. The stock room supplies this solution.

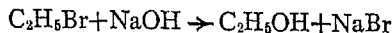
D. Pour 5 cc. of ethyl alcohol into a test tube. Immerse the test tube in a beaker of ice water, and add slowly, drop by drop, about 0.5 cc. of acetyl chloride,  $\text{CH}_3\text{COCl}$ . When all the chloride has been added, allow the mixture to cool a few minutes longer and then add about 1 cc. of a filtered, concentrated solution of sodium chloride. Ethyl acetate,  $\text{CH}_3\text{COOC}_2\text{H}_5$ , which is insoluble in a salt solution, separates on the surface of the liquid and is recognized by its fragrant odor:



Ethyl alcohol may be obtained by the alkaline hydrolysis of ethyl chloride or bromide, as shown by the following experiment:

#### EXPERIMENT 17

##### Conversion of ethyl bromide into ethyl alcohol



*Materials*  $\left\{ \begin{array}{l} 10 \text{ cc. ethyl bromide} \\ \text{Solution of 7 grams of sodium hydroxide dissolved} \\ \text{in 70 cc. of water} \end{array} \right.$

*Procedure.* Pour 10 cc. of ethyl bromide into a 200 cc. flask and add a solution of 7 grams of sodium hydroxide dissolved in 70 cc. of water. The flask is connected to a reflux condenser and the mixture boiled on a wire gauze until it is homogeneous, which will require about 1.5 hours. The apparatus is now disconnected and the mixture poured into a distilling flask and distilled in the ordinary manner. Collect about 20 cc. of the distillate and test for ethyl alcohol by the iodoform reaction (Experiment 16 C, page 81). The residue in the

flask should be evaporated to dryness in an evaporating dish over a water bath and tested for sodium bromide with a dilute solution (1 : 20) of silver nitrate.

The conversion of ethyl bromide into ethyl alcohol consists, then, in the substitution of the hydroxyl group for one atom of bromine. Since ethyl bromide is a monobrom derivative of

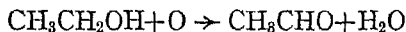
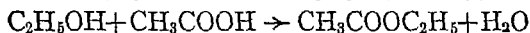
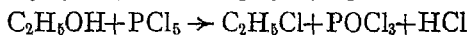
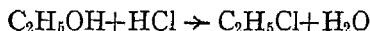
ethane and has the formula  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{Br} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ , it is evident that

the complete structural formula of ethyl alcohol must be

$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ , which is usually written in an abbreviated form

as  $\text{CH}_3\text{CH}_2\text{OH}$  or  $\text{C}_2\text{H}_5\text{OH}$ . This formula is in harmony with its general chemical behavior.

Ethyl alcohol gives characteristic alcohol reactions similar to methyl alcohol, as shown by the following equations:



Ethyl alcohol unites with calcium chloride, forming the compound  $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$ , and hence calcium chloride cannot be used as a dehydrating agent for ethyl alcohol.

**Alcoholic beverages.** There are two classes of alcoholic beverages. Those obtained by fermentation alone contain a low percentage of alcohol. Alcoholic beverages containing a high percentage of alcohol are obtained by distilling fermented liquids and hence are called *distilled liquors*. The efficiency of these beverages depends upon the amount of alcohol they contain.

Distilled liquors such as whisky, brandy, gin, and rum are simply mixtures of alcohol and water, together with small amounts of other substances obtained from the fruits or grain used in their manufacture and which impart the particular flavor to these beverages. Such strong liquors contain from 40 to 60 per cent of alcohol. Light wines such as claret, Rhine, and sauterne, which are made from the fermented juice of grapes, contain about 8 per cent of alcohol. Beer, which is made from fermented malt, contains about 4 per cent of alcohol.

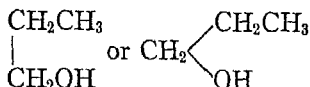
Fusel oil, which is a mixture of the higher homologues of ethyl alcohol, such as the amyl alcohols, is present in the stronger of the alcoholic beverages, but by redistillation and aging this is mostly removed.

**Denatured alcohol.** Ethyl, or grain, alcohol of 95 per cent purity is taxed in the United States at a certain rate per gallon of proof spirit which contains 50 per cent of alcohol by volume. Denatured alcohol is simply ordinary ethyl alcohol to which certain ingredients have been added to render it useless as a beverage. Alcohol adulterated in this manner and which is not intended to be used as a beverage, but only for use in various industries, is not taxed by the government and consequently may be sold cheaper. The substances frequently employed to make alcohol unfit for drinking purposes are methyl alcohol, benzene, and certain pyridine bases.

**Other alcohols.** As we have explained, propane contains hydrogen atoms that have two different relations to the carbon atoms in the molecule. Consequently propane yields two isomeric monochlor derivatives, which are normal propyl chloride and isopropyl chloride. Write the structural formula of these compounds. Corresponding to these isomeric propyl chlorides we should expect to have two isomeric monohydroxy derivatives of propane. Both of them are known. Normal propyl alcohol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , is a colorless liquid which boils at  $97^\circ$ . Isopropyl alcohol,  $\text{CH}_3\text{CHOHCH}_3$ , is also a colorless liquid boiling at  $82^\circ$ .



In order to distinguish these higher alcohols, it is customary to regard them as derived from methyl alcohol by the substitution of one or more of the hydrogen atoms in the methyl group by radicals. Since methyl alcohol is called *carbinol*, normal propyl alcohol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , would be then, *ethyl carbinol*,



and isopropyl alcohol would be *dimethyl carbinol*,  $\begin{array}{c} \nearrow \text{CH}_3 \\ \text{CHOH} \\ \searrow \text{CH}_3 \end{array}$ .

There are two isomeric butanes, and since each of these contains two different sets of hydrogen atoms we should expect these butanes to give four isomeric monohydroxy derivatives. These alcohols with their names and boiling points are given in the table on page 86. The hydrocarbons from which they are derived also are shown. Certain hydrogen atoms in the hydrocarbons are inclosed in circles or squares. This is to indicate where substitution has taken place.

The alcohols that we have considered are divided into three classes. Those containing a  $(\text{CH}_2\text{OH})$  group are called *primary alcohols*. Methyl alcohol, which may be written  $\text{HCH}_2\text{OH}$ , is a primary alcohol. Normal butyl and isobutyl alcohols are also primary alcohols. Alcohols which have a  $(\text{CHOH})$  group, such as methyl ethyl carbinol, are called *secondary alcohols*. Alcohols containing a  $(\text{COH})$  group, such as trimethyl carbinol, are called *tertiary alcohols*.

The different classes of alcohols give characteristic reactions, and hence we are able to ascertain to which class an alcohol belongs by studying its chemical behavior. A primary alcohol when oxidized yields an aldehyde, which on further oxidation gives an acid containing the same number of carbon atoms as the primary alcohol. Secondary alcohols on oxidation give ketones, which on further oxidation yield a mixture of acids

each of which contains a smaller number of carbon atoms than the secondary alcohol. When tertiary alcohols are oxidized, they give a mixture of acids each of which contains a smaller number of carbon atoms than the tertiary alcohol. Aldehydes, ketones, and acids are compounds which will be discussed later.

## BUTYL ALCOHOLS

HYDROCARBONS	ALCOHOLS	BOILING POINT, °C.
$  \begin{array}{cccc}  \text{H} & \text{H} & \text{H} & \text{H} \\    &   &   &   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    &   &   &   \\  \text{H} & \text{H} & \text{H} & \text{H}  \end{array}  $ <p>normal butane</p>	$  \begin{array}{cccc}  \text{H} & \text{H} & \text{H} & \text{H} \\    &   &   &   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} & \text{or} & \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_3 \\   \\ \text{CH}_2\text{OH} \end{array} \\    &   &   &   \\  \text{H} & \text{H} & \text{H} & \text{H}  \end{array}  $ <p>normal butyl alcohol (propyl carbinol)</p>	117
$  \begin{array}{cccc}  \text{H} & \text{H} & \text{H} & \text{H} \\    &   &   &   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    &   &   &   \\  \text{H} & \text{H} & \text{H} & \text{H}  \end{array}  $ <p>normal butane</p>	$  \begin{array}{cccc}  \text{H} & \text{H} & \text{H} & \text{H} \\    &   &   &   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} & \text{or} & \begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{CHOH} \\   \\ \text{CH}_3 \end{array} \\    &   &   &   \\  \text{H} & \text{H} & \text{OH} & \text{H}  \end{array}  $ <p>secondary butyl alcohol (ethyl methyl carbinol)</p>	99
$  \begin{array}{cccc}  \text{H} & \text{H} & \text{H} & \\    &   &   & \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    &   &   & \\  \text{H} & & \text{H} & \\    & &   & \\  \text{H}-\text{C}-\text{H} & & & \\    & & & \\  \text{H} & & &  \end{array}  $ <p>isobutane</p>	$  \begin{array}{cccc}  \text{H} & \text{H} & \text{H} & \\    &   &   & \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} & \text{or} & \begin{array}{c} \text{CH}(\text{CH}_3)_2 \\   \\ \text{CH}_2\text{OH} \end{array} \\    &   &   & \\  \text{H} & & \text{H} & \\    & &   & \\  \text{H}-\text{C}-\text{H} & & & \\    & & & \\  \text{H} & & &  \end{array}  $ <p>isobutyl alcohol (isopropyl carbinol)</p>	106
$  \begin{array}{cccc}  \text{H} & \text{H} & \text{H} & \\    &   &   & \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    &   &   & \\  \text{H} & & \text{H} & \\    & &   & \\  \text{H}-\text{C}-\text{H} & & & \\    & & & \\  \text{H} & & &  \end{array}  $ <p>isobutane</p>	$  \begin{array}{cccc}  \text{H} & \text{OH} & \text{H} & \\    &   &   & \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} & \text{or} & (\text{CH}_3)_3\text{COH} \\    &   &   & \\  \text{H} & & \text{H} & \\    & &   & \\  \text{H}-\text{C}-\text{H} & & & \\    & & & \\  \text{H} & & &  \end{array}  $ <p>tertiary butyl alcohol (trimethyl carbinol)</p>	83



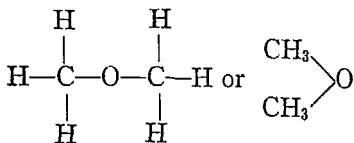
## QUESTIONS

1. What kind of compounds are alcohols?
2. What is meant by destructive distillation?
3. Balance the following equations:
  - a. methyl alcohol + hydrogen chloride  $\rightarrow$ .
  - b. methyl alcohol + phosphorus pentachloride  $\rightarrow$ .
  - c. methyl alcohol + acetic acid  $\rightarrow$ .
  - d. methyl alcohol + acetyl chloride  $\rightarrow$ .
  - e. methyl alcohol + sodium  $\rightarrow$ .
  - f. methyl alcohol oxidized  $\rightarrow$ .
4. How is the structural formula of methyl alcohol determined?
5. Write equations showing how ethyl alcohol may be prepared from cane sugar and from starch.
6. What is absolute alcohol and how is it prepared?
7. How do you test for water in alcohol?
8. Explain how ethyl bromide may be converted into ethyl alcohol. Give the equations.
9. In preparing a substance which is anhydrous, how do you arrange the apparatus to prevent the entrance of atmospheric moisture?
10. Explain, with equations, how ethyl alcohol behaves when treated with sodium, when oxidized, and when treated with acetyl chloride.
11. What are the principal uses of methyl and ethyl alcohols?
12. What are enzymes?
13. How many isomeric monohydroxy derivatives do ethane, propane, and the butanes yield?
14. Write the structural formulas of the following substances: carbinol; methyl carbinol; isopropyl carbinol.
15. What is meant by primary, secondary, and tertiary alcohols? How are these substances distinguished?
16. Write the following series of reactions in outline equations:
  - a. cane sugar  $\rightarrow$  ethylene dichloride.
  - b. starch  $\rightarrow$  benzene.
17. From what hydrocarbons are the following alcohols derived: ethyl alcohol; isopropyl alcohol; normal butyl alcohol? To what classes of alcohols do these substances belong?

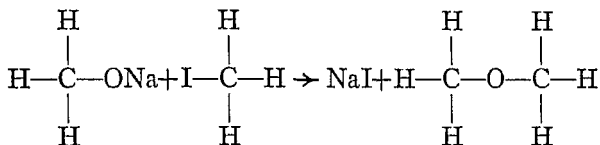
## CHAPTER FIVE

### ETHERS AND SULFUR COMPOUNDS

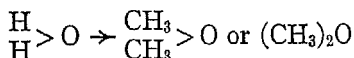
**Ethers** are compounds which contain two radicals, such as methyl groups, united by one atom of oxygen. The simplest ether would therefore be *dimethyl ether*, or, as it is usually called, *methyl ether*:



This substance is a gas which may be liquefied at  $-23.6^\circ$ . It may be prepared by the interaction of sodium methoxide and methyl iodide:



Since the structural formulas of sodium methoxide and methyl iodide are as represented in the equation above, it follows that methyl ether must have the structural formula assigned to it. It may be regarded as derived from methane by substituting the methoxide group ( $\text{CH}_3\text{O}$ ) for one atom of hydrogen. Again, it may be looked upon as a derivative of water obtained by substituting the two hydrogen atoms in water by methyl groups:

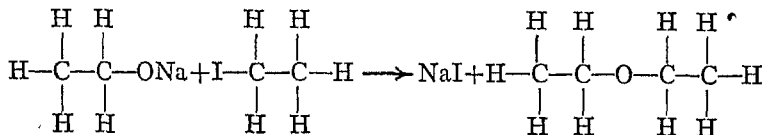


Since water may be considered an oxide, we may accordingly regard methyl ether as dimethyl oxide. In the following table are given the complete and abbreviated structural formulas of a few of the simpler ethers, with their boiling points:

## ETHERS

NAME	STRUCTURAL FORMULA		BOILING POINT, °C.
	Complete	Abbreviated	
Dimethyl ether	<pre>       H   H             H — C — O — C — H                   H   H           </pre>	$(\text{CH}_3)_2\text{O}$	-23.6
Diethyl ether	<pre>       H   H   H   H                     H — C — C — O — C — C — H                           H   H   H   H           </pre>	$(\text{C}_2\text{H}_5)_2\text{O}$	34.6
Dipropyl ether	<pre>       H   H   H   H   H   H                             H — C — C — C — O — C — C — C — H                                   H   H   H   H   H   H           </pre>	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{O}$	90.7
Diisopropyl ether	<pre>           H   H   H                           H — C — C — C — H                               H   O   H                               H   O   H                           H — C — C — C — H                               H   H   H           </pre>	$\left(\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} > \text{CH} \right)_2\text{O}$	69

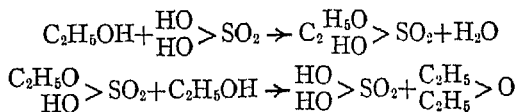
These ethers, therefore, form a series of compounds the second member of which is *diethyl ether*. This compound is usually spoken of simply as ether. It may be prepared by treating sodium ethylate with ethyl iodide:



Ether is, therefore, diethyl oxide,  $(C_2H_5)_2O$ . The usual laboratory method of preparation consists in distilling a mixture of alcohol and sulfuric acid heated to a temperature of  $140^\circ$ . Ethyl hydrogen sulfate,  $\begin{smallmatrix} C_2H_5O \\ HO \end{smallmatrix} > SO_2$ , or  $C_2H_5.HSO_4$ , is formed as an intermediate product, but this then reacts with the alcohol present to form ether and sulfuric acid. By adding a new supply of alcohol to the mixture, more ether is generated. This is known as the *continuous process*. What product would be formed by heating a mixture of alcohol and sulfuric acid, prepared in the proper proportions, to a temperature of  $100^\circ$ ? To a temperature of  $170^\circ$ ?

## EXPERIMENT 18

Preparation of ether,  $C_2H_5 > O$   
(Ethyl oxide)  $C_2H_5$



Materials  $\left\{ \begin{array}{l} 50 \text{ cc. concentrated sulfuric acid} \\ 100 \text{ cc. absolute alcohol} \end{array} \right.$

NOTE. As ether is very volatile and inflammable, considerable care should be exercised in performing this experiment. Vessels containing ether should always be carefully stoppered and not allowed to stand near flames or in a warm place.

*Procedure.* Arrange an apparatus as shown in Figure 12, page 92. The 500 cc. distilling flask *A* is connected to a condenser which is joined to a filtering flask *B* by means of an adapter *C*. The side tube of the filtering flask is connected to a long rubber tube *D* which reaches nearly to the floor. This serves to conduct away from the desk the ether vapors escaping from the filtering flask. Flask *A* is fitted with a good two-holed cork stopper. Through one hole is passed a thermometer *E*, and through the other hole is inserted a glass tube *F* which is drawn out to a fairly fine bore at the lower end. The upper end of the tube *F* is connected to a large dropping funnel *H* by means of rubber tubing.

Disconnect the distilling flask *A*, and pour into it 60 cc. of abso-

lute alcohol. Add to this with constant shaking and cooling 50 cc. of concentrated sulfuric acid. The whole apparatus is again adjusted.

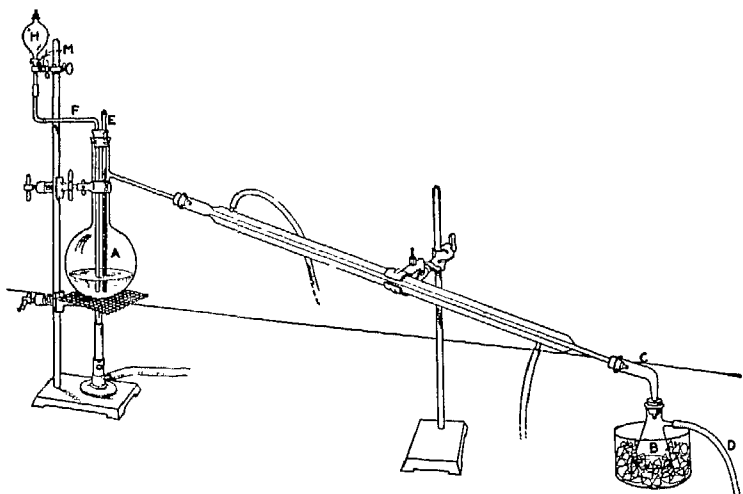


Figure 12

The thermometer *E* is now so adjusted that the mercury bulb dips just below the surface of the mixture in the flask *A*. Close the stopcock *M* and pour into the dropping funnel *H* 40 cc. of absolute alcohol. Immerse the filtering flask *B* in a large beaker containing ice and water. See that the apparatus is arranged properly and that all connections are secure.

An asbestos wire gauze is placed under the flask *A*, and the mixture of alcohol and sulfuric acid is heated gradually until the thermometer shows a temperature of  $140^{\circ}$ . By carefully opening the stopcock *M*, the alcohol is allowed to drop gradually into the heated mixture in *A*, at about the same rate as the ether distils over. The temperature in the flask should be maintained constant between  $140^{\circ}$  and  $145^{\circ}$ . The reaction product prepared in this manner contains besides ether small amounts of alcohol, water, and sulfurous acid.

The ether may be purified in the following manner: Pour the ether into a separating funnel and add a solution consisting of 2 grams of sodium hydroxide dissolved in about 20 cc. of water. The mixture is shaken thoroughly, allowed to settle, and the lower layer of sodium



hydroxide solution drawn off and discarded. The alkali solution neutralizes the acid present and dissolves the alcohol, leaving, after separation, only the ether, which is now saturated with water. A saturated solution of sodium chloride is now added, the quantity of which should be about one half the volume of the ether. (Saturated sodium chloride solution may be obtained from the stock room.) The lower layer is again separated and discarded. The sodium chloride renders the ether much less soluble in water, and consequently a larger amount may be separated out from the mixture. The ether is now poured into a dry bottle, and to it are added about a dozen small pieces (pea size) of granulated anhydrous calcium chloride. The bottle should be well stoppered and allowed to stand several hours. The ether is now poured into a small, dry distilling flask which is connected to a condenser. The flask is fitted with a cork stopper through which passes a thermometer so adjusted as to determine the boiling point of the ether. How? A water bath heated to about  $80^{\circ}$  is placed under the flask and the ether distilled over into a dry receiver arranged as in the previous distillation of the impure ether. Weigh the product you have obtained and calculate the percentage yield. The boiling point of ether is  $34.6^{\circ}$ . Preserve a specimen.

The ether thus prepared still contains traces of alcohol and water, from which it may be separated by further treatment with metallic sodium.

Ether is a colorless liquid which is very inflammable, and when working with ethereal solutions one must be very careful to have no lighted burners near by. It is a valuable anesthetic, and is used as a solvent for organic substances. It is frequently used to extract fats, oils, and compounds from mixtures in which they are present.

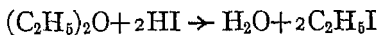
#### EXPERIMENT 19

##### Extraction with ether

*Procedure.* Place 1 gram of powdered salicylic acid in a 500 cc. beaker, and add to it about 100 cc. of water. The contents of the beaker are now stirred thoroughly and filtered. The filtrate, which is a salicylic acid solution, is poured into a separating funnel. Add to it 30 cc. of ether and 20 cc. of a saturated sodium chloride solution; shake, and allow the mixture to settle. The salicylic acid is taken

up by the ether and is now present in the top ethereal layer. The layers are separated and the top layer poured into a beaker, which is now immersed in a water bath previously heated to about 80°. (See that no lighted burners are near the water bath.) When all the ether has evaporated, the salicylic acid will remain as a white solid deposited on the side and bottom of the beaker.

The chemical behavior of diethyl ether is characteristic of other ethers. It contains no hydroxyl group and is, therefore, not acted upon by sodium, or acetyl chloride. It reacts with hydrogen iodide to form ethyl iodide:



The methods of preparation and characteristic reactions of dipropyl ether and other higher members of this series of ethers are similar to those of dimethyl and diethyl ethers.

*Mixed ethers.* Ethers such as dimethyl and diethyl ethers are known as *simple ethers* because they contain two radicals which are identical. Mixed ethers are those which contain different radicals. They may be prepared in a manner similar to the preparation of methyl ether, except that compounds containing different radicals are used. For example, methyl ethyl ether may be prepared by the interaction of sodium ethylate and methyl iodide:



In a like manner we may prepare ethers containing other radicals. The table on page 95 contains the complete and abbreviated structural formulas of a few mixed ethers.

These compounds give reactions similar to the simple ethers. The general formula of ethers is, then,  $\text{ROR}'$ , where R and R' may be the same or different radicals.

The important radicals we have studied so far are the methyl, ethyl, propyl, and isopropyl groups. The student should endeavor to understand the behavior of these alkyl radicals, as they determine to a considerable extent the behavior and properties of a compound.

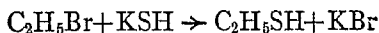
## MIXED ETHERS

NAME	STRUCTURAL FORMULA		BOILING POINT, °C.
	Complete	Abbreviated	
Methyl ethyl ether	$  \begin{array}{ccccc}  & \text{H} & & \text{H} & \text{H} \\  &   & &   &   \\  \text{H} & - \text{C} & - \text{O} & - \text{C} & - \text{C} - \text{H} \\  &   & &   &   \\  & \text{H} & & \text{H} & \text{H}  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 \\  > \text{O} \\  \text{C}_2\text{H}_5  \end{array}  $	11
Normal propyl methyl ether	$  \begin{array}{ccccccc}  & \text{H} & \text{H} & \text{H} & & \text{H} & \\  &   &   &   & &   & \\  \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{O} & - \text{C} & - \text{H} \\  &   &   &   & &   & \\  & \text{H} & \text{H} & \text{H} & & \text{H} &  \end{array}  $	$  \begin{array}{c}  \text{CH}_3\text{CH}_2\text{CH}_2 \\  > \text{O} \\  \text{CH}_3  \end{array}  $	50
Ethyl propyl ether	$  \begin{array}{ccccccc}  & \text{H} & \text{H} & & \text{H} & \text{H} & \text{H} \\  &   &   & &   &   &   \\  \text{H} & - \text{C} & - \text{C} & - \text{O} & - \text{C} & - \text{C} & - \text{C} - \text{H} \\  &   &   & &   &   &   \\  & \text{H} & \text{H} & & \text{H} & \text{H} & \text{H}  \end{array}  $	$  \begin{array}{c}  \text{C}_2\text{H}_5 \\  > \text{O} \\  \text{CH}_3\text{CH}_2\text{CH}_2  \end{array}  $	63

## SULFUR COMPOUNDS

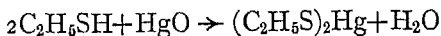
A large number of organic sulfur compounds have been prepared synthetically. These organic sulfur compounds have formulas similar to the corresponding oxygen compounds. The thioalcohols (mercaptans) and thioethers are regarded as derivatives of hydrogen sulfide,  $\text{H}_2\text{S}$ .

**Ethyl mercaptan**,  $\text{C}_2\text{H}_5\text{SH}$ , is prepared by the interaction of an alkyl halide and an alcoholic solution of potassium hydrosulfide:

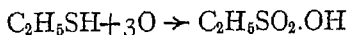


This reaction is similar to that used in preparing ethyl alcohol from ethyl bromide (Experiment 17). Ethyl mercaptan is a colorless liquid which boils at  $36^\circ$ , and has a very disagreeable odor. Ethyl mercaptan and other substances having similar formulas are called *mercaptans* because they form compounds

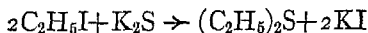
with mercury (*mercurium captans*). Thus, when ethyl mercaptan is treated with mercuric oxide it yields mercuric mercaptide  $(C_2H_5S)_2Hg$ :



When oxidized with nitric acid the mercaptans yield sulfonic acids, which are compounds containing the group  $(SO_2.OH)$ . Thus, ethyl mercaptan yields ethyl sulfonic acid,  $C_2H_5SO_2.OH$ :

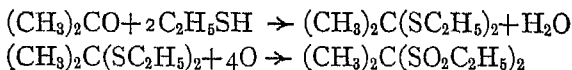


Ethyl sulfide,  $(C_2H_5)_2S$ , is obtained by treating an alkyl halide with potassium sulfide:



Ethyl sulfide is a colorless liquid which boils at  $91^\circ$ . Like most other thioethers it has a disagreeable odor. When oxidized, ethyl sulfide is converted into ethyl sulfone,  $(C_2H_5)_2SO_2$ .

**Sulfonal**,  $(CH_3)_2C(SO_2.C_2H_5)_2$ , is prepared by treating acetone,  $(CH_3)_2CO$ , with ethyl mercaptan in the presence of hydrogen chloride. These substances react, forming the condensation product  $(CH_3)_2C(SC_2H_5)_2$ , which when oxidized yields the disulfone sulfonal:



Sulfonal is used medicinally as a soporific.

*Trional*,  $\overset{CH_3}{\underset{C_2H_5}{C}} > C(SO_2C_2H_5)_2$ , which also is a soporific, is prepared in a similar manner from ethyl methyl ketone,  $C_2H_5COCH_3$ .

## QUESTIONS

1. What kind of compounds are ethers?
2. Show by structural formulas the analogy between water, inorganic oxides, and organic oxides.
3. Explain how dimethyl ether may be regarded as a hydrocarbon derivative.
4. Write an equation which will show the structure of dimethyl ether.
5. Give equations showing the preparation of ethyl ether from ethyl alcohol and sulfuric acid. Why is this method called the continuous process?
6. Dimethyl ether is isomeric with ethyl alcohol. By what reactions could you distinguish these compounds?
7. Two compounds have the molecular formula  $C_3H_8O$ . When treated with hydrogen iodide, No. 1 gives methyl iodide, ethyl iodide, and water, while No. 2 gives propyl iodide and water. Write the structural formula of these compounds and the equations showing the above reactions.
8. For what purposes is ether used?
9. What is meant by "extraction with ether"?
10. Write the following series of reactions in outline equations:
  - a. ethane  $\rightarrow$  ethyl alcohol  $\rightarrow$  ethyl ether  $\rightarrow$  ethyl iodide  $\rightarrow$  normal butane.
  - b. methane  $\rightarrow$  methyl alcohol  $\rightarrow$  methyl iodide  $\rightarrow$  ethylene  $\rightarrow$  ethyl alcohol.
11. What is meant by a "general formula"? Write a general formula for ethers.
12. What are mixed ethers and how are they prepared?
13. What are mercaptans and thioethers?
14. How is ethyl mercaptan obtained?

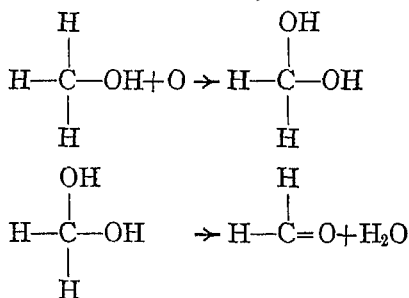
## CHAPTER SIX

### ALDEHYDES AND KETONES

**Aldehydes** are compounds which contain the aldehyde group  $\left[ \begin{array}{c} \text{H} \\ | \\ \text{C}=\text{O} \end{array} \right.$  or CHO. They form a homologous series of compounds

and may be regarded as derived from the paraffin hydrocarbons by the substitution of the aldehyde group (CHO) for one atom of hydrogen. The table on page 99 contains the complete and abbreviated structural formulas of a few aldehydes and their boiling points, and also the hydrocarbons from which they are derived. The general formula for aldehydes is, then, RCHO, where R represents an atom of hydrogen or a radical.

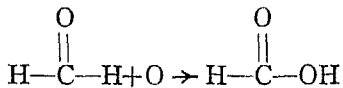
**Formaldehyde**, HCHO, is the first member of this series of compounds. It is not derived from a hydrocarbon, but since it contains the aldehyde group and has the structure of these compounds it is conveniently included in this series. It may be prepared by the oxidation of methyl alcohol:



Formaldehyde is a gas which has a peculiar odor and may be condensed to a liquid boiling at  $-21^{\circ}$ . *Formalin* is an aqueous solution of formaldehyde containing about 40 per cent of the gas. It is used commercially as an antiseptic, disinfectant, and food preservative. When oxidized, formaldehyde yields formic

acid,  $\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{C}-\text{OH} \end{array}$ , or HCOOH, just as other aldehydes yield

their corresponding acids when oxidized:



Formaldehyde, like other aldehydes, is therefore an energetic reducing agent.

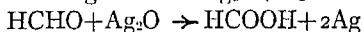
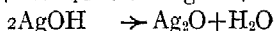
## ALDEHYDES

HYDROCARBONS	STRUCTURAL FORMULA		BOILING POINT, °C.
	Complete	Abbreviated	
	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}=\text{O} \end{array}$ formaldehyde	HCHO	-21
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$ methane	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}=\text{O} \\   \\ \text{H} \end{array}$ acetaldehyde	CH <sub>3</sub> CHO	20.8
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ ethane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}=\text{O} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$ propionic aldehyde	CH <sub>3</sub> CH <sub>2</sub> CHO	49
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ propane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}=\text{O} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ butyric aldehyde	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO	74
	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \\   \\ \text{H}-\text{C}=\text{O} \end{array}$ butyric aldehyde (iso)	(CH <sub>3</sub> ) <sub>2</sub> CHCHO	63

## EXPERIMENT 20

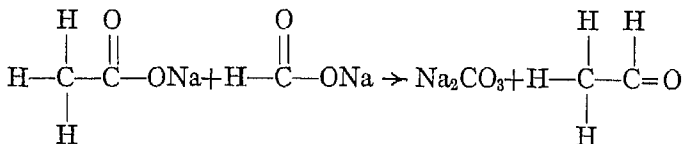
## Silver mirror test for formaldehyde

To 5 cc. of dilute silver nitrate solution (1 : 20) add a dilute ammonia solution (1 : 20) until the slight precipitate formed is just dissolved. Add to this ammonia-silver nitrate solution about 1 cc. of a solution of formalin (formaldehyde), and warm. A silver mirror is deposited on the side of the test tube, while the formaldehyde is oxidized to formic acid,  $\text{HCOOH}$ :



By evaporating an aqueous solution of formaldehyde a polymer known as *meta formaldehyde*,  $(\text{HCHO})_x$ , is obtained. The molecular weight of this substance is not known. What are polymers and what is meant by polymerization?

**Acetaldehyde**,  $\text{CH}_3\text{CHO}$ , is the second member of this series of aldehydes. It may be prepared by distilling a dry mixture consisting of a salt of acetic acid, such as sodium acetate,  $\text{CH}_3\text{COONa}$ , with a salt of formic acid, like sodium formate,  $\text{HCOONa}$ ,



This method gives better results, however, when the calcium salts of these acids are used. The distillation of a mixture of the calcium salt of formic acid and the calcium salt of some other acid is a method which is frequently used in the preparation of aldehydes.

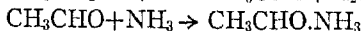
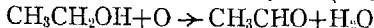
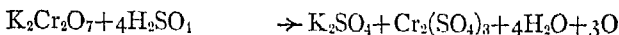
The oxidation of primary alcohols furnishes also another general method for preparing aldehydes. Thus, acetaldehyde may be prepared easily by oxidizing ethyl alcohol. Since acetaldehyde boils at a low temperature and is rather volatile, it may be preserved conveniently by treating it with ammonia,



thus forming the crystalline addition product aldehyde ammonia,  $\text{CH}_3\text{CHO} \cdot \text{NH}_3$ , from which it may be obtained by treatment with dilute sulfuric acid.

## EXPERIMENT 21

## Preparation of acetaldehyde ammonia



<i>Materials</i>	{	Solution of 75 cc. of concentrated sulfuric acid dissolved in 300 cc. of water
		125 cc. ethyl alcohol (95 per cent)
		100 grams potassium dichromate
		50 cc. water

*Procedure.* Arrange an apparatus as shown in Figure 13, page 102. The round flask *A*, which has a capacity of about 1.5 liters, is connected to an elevated condenser. The condenser is connected to the filtering flask *F*. The beaker *B* contains about 400 cc. of tap water and is connected to the condenser by means of a rubber tube which is joined to a piece of bent glass tubing. The pinchcock *H* prevents the water in the beaker *B* from flowing out. *M* is a safety tube which reaches to the bottom of flask *A*.

The materials which are to be placed in flask *A* are now mixed in separate flasks in the following manner: In a liter flask add gradually, with constant shaking and cooling, 75 cc. of concentrated sulfuric acid to 300 cc. of water. To the cold mixture add gradually, with cooling, 125 cc. of ethyl alcohol (95 per cent). When the mixture has reached the room temperature, pour it into a dropping funnel. Into another liter flask pour 100 grams of coarse, granulated potassium dichromate, and add 50 cc. of water. Immerse the flask in a bath of ice and water; add gradually from the dropping funnel, with frequent shaking, the mixture previously prepared.

When the materials have been mixed in the manner described, disconnect flask *A*, and pour into it the mixture consisting of sulfuric acid, water, alcohol, and potassium dichromate solution. The water in the beaker *B* is heated to 40° and allowed to flow into the condenser

by opening the pinchcock at *H*. When the water in the condenser seems to have the same temperature as the water in the beaker, close

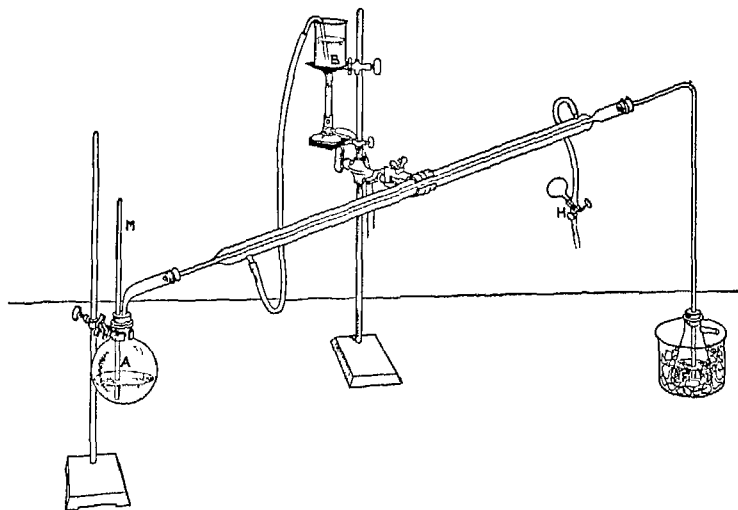


Figure 13

the pinchcock *H*. The temperature of the water in the condenser is maintained at  $40^{\circ}$  by allowing the water in the beaker *B* to flow into the condenser at frequent intervals.

Pour about 70 cc. of ether into the filtering flask *F*, which should be immersed in a beaker containing ice and water.

Adjust the entire apparatus and see that all connections are tight. Flask *A*, containing the materials, is warmed gently. If the action becomes too violent, the flame must be removed quickly and the flask cooled by placing a bath of ice water under flask *A* until the flask is partly submerged. When the action has subsided somewhat, remove the bath, dry the flask with a towel, and warm again. By carefully heating, or cooling, the mixture can be made to boil gently. After boiling in this manner about 15 minutes, the mixture may be boiled carefully by means of a medium-sized flame until all the aldehyde has distilled over. This will require about 1 hour and can be determined by removing the stopper from the flask and noticing if the odor of aldehyde is appreciably perceptible. The apparatus is now disconnected, but the receiver containing the

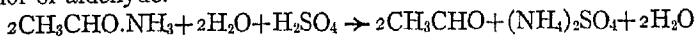
etheral solution of the aldehyde is still allowed to remain immersed in the ice water.

Heat about 50 cc. of concentrated ammonia water in an Erlenmeyer flask. Allow the gas to generate slowly, and pass it through a calcium chloride tube containing soda lime to dry it, and then through a medium-wide tube into the ethereal solution of the aldehyde. Pass the gas about 15 minutes.

Disconnect the apparatus and filter the crystals of aldehyde ammonia. Wash with a small quantity of ether (see that no flames are near by) and dry on filter paper. Preserve a specimen in a sealed tube and perform Experiment A, with another portion of the yield. As the crystals of aldehyde ammonia decompose on standing in the air, they should be preserved in a bottle which is stoppered securely or in a sealed tube.

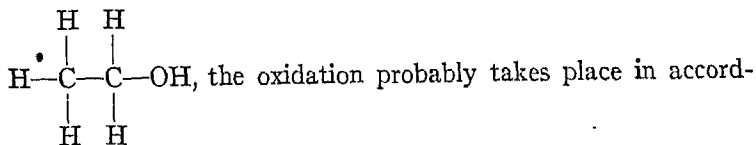
NOTE. In preparing aldehyde ammonia, the apparatus is arranged as shown in the figure. An elevated condenser which contains water heated to a temperature of  $40^{\circ}$  is used, because with this arrangement of the apparatus the aldehyde distils over easily while the alcohol and water do not distil over but are condensed and refluxed back into the flask. Thus, by arranging the apparatus in this manner, the aldehyde is separated from the other volatile substances which are present in the reacting mixture.

A. Place a few of the crystals of aldehyde ammonia in a test tube, add 4 cc. of a solution of sulfuric acid (1:1), and heat. Notice the odor of aldehyde.

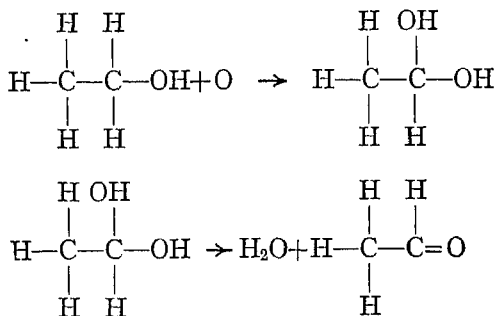


Acetaldehyde is a colorless liquid which boils at  $20.8^{\circ}$  and has a peculiar penetrating odor. It is soluble in water, alcohol, and ether.

*Structure.* As shown by Experiment 21, acetaldehyde may be prepared by the oxidation of ethyl alcohol. As ethyl alcohol is monohydroxy ethane and has the structural formula



the oxidation probably takes place in accordance with the following equations:



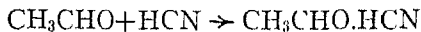
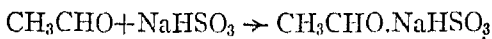
An intermediate compound,  $\begin{array}{c} \text{H} \quad \text{OH} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ , which is probably

formed, contains two hydroxyl groups united to one carbon atom. As this is an unstable structure, this compound is immediately decomposed into water and acetaldehyde. If this is the true mechanism of this reaction, then in order to represent the carbon atoms as having a valence of four we should have to assign to

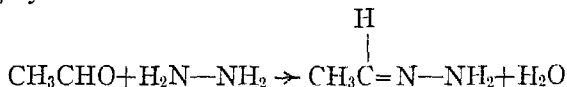
acetaldehyde the structural formula  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}=\text{O} \\ | \\ \text{H} \end{array}$  as the one

which would appear to be most probable. Acetaldehyde, then, is to be considered as methane in which one hydrogen atom has been substituted by the aldehyde group. This formula is in harmony with the general chemical behavior of this compound.

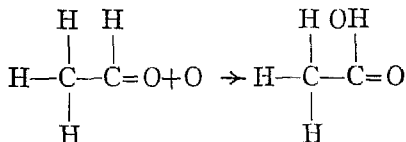
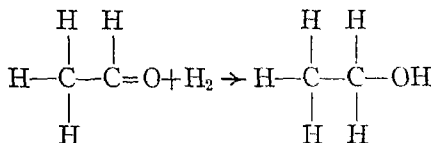
*Reactions of acetaldehyde.* Acetaldehyde gives reactions which are characteristic of aldehydes. It forms addition products when treated with various compounds. The interaction of acetaldehyde and ammonia yields the white crystalline compound aldehyde ammonia. When treated with sodium hydrogen sulfite or hydrogen cyanide, similar addition products are obtained:



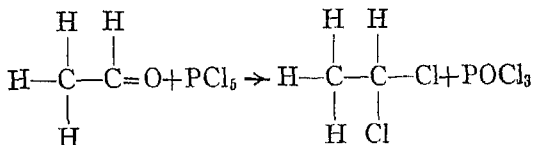
Acetaldehyde reacts with hydrazine,  $\begin{array}{c} \text{NH}_2 \\ | \\ \text{NH}_2 \end{array}$ , or its derivatives, yielding hydrazones:



When reduced, acetaldehyde yields ethyl alcohol, and when oxidized it is converted into acetic acid,  $\text{CH}_3\text{COOH}$ :



What compound would be formed by the reduction of propionic aldehyde? By the oxidation of propionic aldehyde? When phosphorus pentachloride reacts with acetaldehyde, the compound ethylidene chloride is obtained:

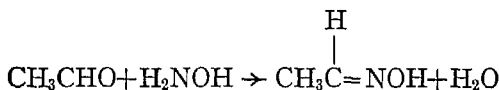


How would ethyl alcohol behave when treated with phosphorus pentachloride? What substance is isomeric with ethylidene chloride?

Aldehydes react with hydroxylamine,  $\text{NH}_2\text{OH}$ , forming com-

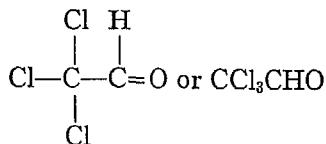
pounds known as *aldoximes*. Thus, when acetaldehyde is treated

with hydroxylamine, acetaldoxime,  $\text{CH}_3\overset{\text{H}}{\underset{|}{\text{C}}}=\text{NOH}$ , is obtained :

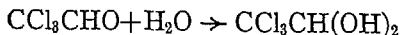


When acetaldehyde is treated with a few drops of concentrated sulfuric acid, a rather explosive action occurs and a pleasant-smelling liquid known as *paraldehyde* is obtained. It is a polymer of acetaldehyde, having the molecular formula  $(\text{C}_2\text{H}_4\text{O})_3$ , and is used in medicine as a soporific, — that is, a substance which produces sleep. *Metaldehyde*,  $(\text{C}_2\text{H}_4\text{O})_3$ , a crystalline polymer, is obtained by the action of acids on acetaldehyde at low temperatures. Acetaldehyde, like many other members of this series, when warmed with alkalis is converted into a brown, resinous substance which is a polymer of acetaldehyde.

When acetaldehyde is treated with chlorine in dilute solution, the three hydrogen atoms in the methyl group are replaced by chlorine, forming the compound trichlor aldehyde :



Trichlor aldehyde is a liquid which boils at  $97^\circ$  and is commonly called *chloral*. It is prepared on a large scale from ethyl alcohol by reactions which are somewhat complicated. Chloral reacts with water, forming chloral hydrate,  $\text{CCl}_3\text{CH}(\text{OH})_2$ , which is used medicinally as a soporific :



The higher members of this series of aldehydes are prepared by reactions similar to those used in making acetaldehyde.

They give characteristic aldehyde reactions. The names of these aldehydes are usually derived from the acids which they yield when oxidized. For example, formaldehyde gives formic acid, and acetaldehyde yields acetic acid.

## QUESTIONS

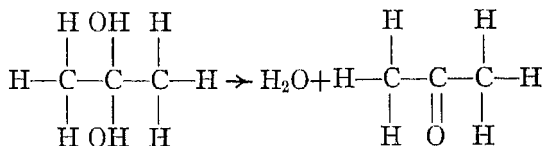
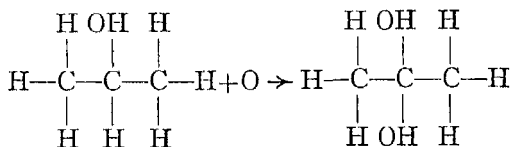
1. What characteristic group do the aldehydes contain?
2. From what hydrocarbon is acetaldehyde derived?
3. How is acetaldehyde ammonia prepared in the laboratory?
4. How do you test for aldehydes?
5. Explain, with equations, two general methods used for preparing aldehydes.
6. Complete the following reactions:
  - a. acetaldehyde + hydrogen  $\rightarrow$ .
  - b. acetaldehyde + oxygen  $\rightarrow$ .
  - c. acetaldehyde + phosphorus pentachloride  $\rightarrow$ .
  - d. acetaldehyde + silver oxide  $\rightarrow$ .
  - e. acetaldehyde + ammonia  $\rightarrow$ .
7. Reactions in outline:
  - a. methane  $\rightarrow$  formaldehyde.
  - b. ethane  $\rightarrow$  acetaldehyde.
  - c. acetaldehyde  $\rightarrow$  ethyl alcohol  $\rightarrow$  ethylene dibromide.
  - d. sodium acetate  $\rightarrow$  acetaldehyde  $\rightarrow$  ethyl chloride.
8. What is chloral hydrate? For what purposes is it used?
9. Write equations showing the preparation of propionic aldehyde.

## KETONES

**Ketones** are compounds which contain the ketone, or carbonyl, group ( $C=O$ ).

A few of these compounds are given in the table on the following page. These ketones are usually named in accordance with the radicals which they contain.

**Dimethyl ketone**,  $(CH_3)_2CO$ , the first member of this series, is commonly called *acetone*. Acetone occurs in normal urine in small quantities. In certain diseases, such as diabetes, the quantity of acetone is considerably increased. Acetone is one of the products formed in the destructive distillation of wood. What is meant by "destructive distillation"? Acetone may be prepared by the oxidation of isopropyl alcohol. It is believed that the reaction takes place in the following manner:



## KETONES

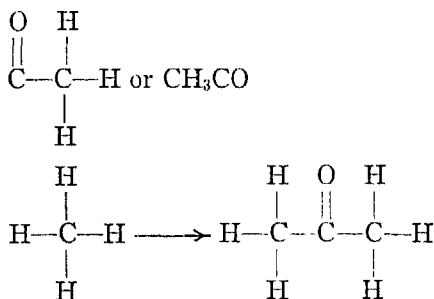
NAME	STRUCTURAL FORMULA		BOILING POINT, °C.
	Complete	Abbreviated	
Dimethyl ketone	$  \begin{array}{c} \text{H} \text{ O} \text{ H} \\   \quad    \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}  $	$(\text{CH}_3)_2\text{CO}$	56.5
Diethyl ketone	$  \begin{array}{c} \text{H} \text{ H} \text{ O} \text{ H} \text{ H} \\   \quad   \quad    \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \text{ H} \text{ H} \text{ H} \end{array}  $	$(\text{C}_2\text{H}_5)_2\text{CO}$	103
Dipropyl ketone	$  \begin{array}{c} \text{H} \text{ H} \text{ H} \quad \text{H} \text{ H} \text{ H} \\   \quad   \quad   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad    \quad   \quad   \quad   \\ \text{H} \text{ H} \text{ H} \text{ O} \text{ H} \text{ H} \text{ H} \end{array}  $	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CO}$	144
Diisopropyl ketone	$  \begin{array}{c} \text{H} \text{ H} \text{ H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{C}=\text{O} \quad \text{H} \\   \quad   \quad   \\ \text{H} \quad \text{C} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \text{ H} \text{ H} \end{array}  $	$(\text{CH}_3)_2\text{CHCOCH}_3$	125



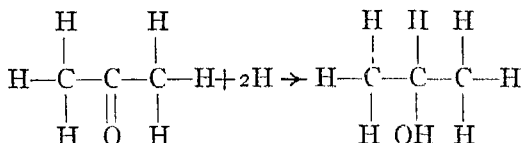
As shown by the equations, only the secondary alcohol group (CHOH) is affected by the oxidation. This group absorbs one atom of oxygen, giving a compound in which there are two hydroxyl groups united to one carbon atom. As this is an unstable condition, this substance is immediately decomposed into water and acetone. Acetone consists, then, of two methyl groups united to a carbonyl group.

Acetone is a colorless liquid which boils at  $56.5^{\circ}$ . It is an excellent solvent for many organic compounds.

*Structure.* Acetone may be considered as derived from propane by the substitution of one atom of oxygen for two hydrogen atoms. It may also be regarded as derived from methane by replacing one hydrogen atom with the acetyl group

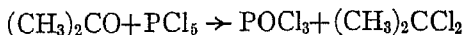
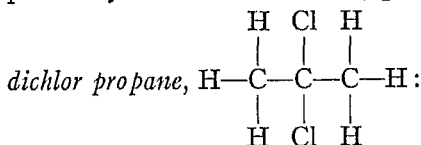


The structural formula of acetone represents its general chemical behavior. Acetone is obtained by the oxidation of isopropyl alcohol,  $\text{CH}_3\text{CHOHCH}_3$ , and when acetone is reduced with hydrogen it is converted into isopropyl alcohol:



The presence of the carbonyl group in acetone is shown by its reaction with phosphorus pentachloride. When acetone reacts with phosphorus pentachloride, the one atom of oxygen is re-

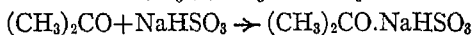
placed by two chlorine atoms, giving the compound called *beta*



*Reactions of ketones and aldehydes.* Acetaldehyde reacts with sodium hydrogen sulfite or hydrogen cyanide, yielding addition products, such as  $\text{CH}_3\text{CHO} \cdot \text{NaHSO}_3$  and  $\text{CH}_3\text{CHO} \cdot \text{HCN}$ . Acetone forms similar addition products when treated with these substances. Thus, the interaction of acetone and hydrogen cyanide yields the addition product  $\text{CH}_3\text{COCH}_3 \cdot \text{HCN}$ . When treated with sodium hydrogen sulfite, acetone forms the crystalline compound  $\text{CH}_3\text{COCH}_3 \cdot \text{NaHSO}_3$ .

## EXPERIMENT 22

### Preparation of acetone sodium hydrogen sulfite

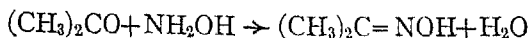


*Materials* { Saturated solution of sodium bisulfite  
15 cc. acetone

*Procedure.* Prepare a saturated solution of sodium bisulfite by treating 20 grams of the salt with about 25 cc. of warm water. Stir the solution a few minutes, and filter. Cool the solution, and pour about 20 cc. of it into a beaker. Add 15 cc. of acetone. Immerse the beaker in a mixture of ice and water, and stir the mixture. When the addition product has crystallized, filter, and dry on filtering paper. This compound decomposes somewhat on standing in the open air, and consequently should be preserved in a sealed tube or in a well-stoppered bottle and not allowed to stand in the open air any considerable length of time. Preserve a specimen.

Aldehydes and ketones when treated with hydroxylamine yield compounds known as *oximes*. Acetaldehyde reacts with hydroxylamine, yielding acetaldoxime,  $\text{CH}_3\text{CH}=\text{NOH}$ . The

interaction of acetone and hydroxylamine gives dimethyl ketoxime,  $(\text{CH}_3)_2\text{C}=\text{NOH}$ :

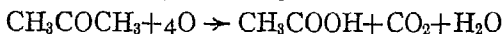
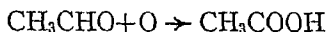


The fact that acetone gives certain reactions similar to acetaldehyde is to be expected, since both compounds have a similar

structure. Acetaldehyde,  $\begin{array}{c} \text{CH}_3-\text{C}=\text{O} \\ | \\ \text{H} \end{array}$ , contains a carbonyl group

united to a methyl group and one hydrogen atom, while acetone,  $\begin{array}{c} \text{CH}_3-\text{C}=\text{O} \\ | \\ \text{CH}_3 \end{array}$ , has two methyl groups united to a carbonyl group.

In certain respects the chemical behaviors of aldehydes and ketones are different. When oxidized, acetaldehyde yields acetic acid, which contains the same number of carbon atoms as acetaldehyde. Acetone when oxidized gives a mixture of acids, each of which contains a smaller number of carbon atoms than acetone:



Acetaldehyde unites easily with ammonia, whereas acetone does not. When treated with reducing agents, acetaldehyde yields a primary alcohol and acetone gives a secondary alcohol. Write the equations.

The reactions of acetaldehyde and acetone illustrate in a general manner the chemical behavior of aldehydes and ketones. In general the reactions of the higher ketones are similar to those of acetone.

**Mixed ketones** are ketones containing different radicals. They may be prepared by distilling a mixture of the calcium salts of different acids. For instance, methyl ethyl ketone may be obtained by distilling a mixture of calcium acetate,  $(\text{CH}_3\text{COO})_2\text{Ca}$ , and calcium propionate,  $(\text{C}_2\text{H}_5\text{COO})_2\text{Ca}$ . This reaction may be understood more easily if, in writing the equa-



## QUESTIONS

1. Write a general formula for ketones.
2. Write the structural formula of acetone and of ethyl methyl ketone.
3. Complete the following reactions :
  - a. isopropyl alcohol + oxygen  $\rightarrow$ .
  - b. acetone + sodium hydrogen sulfite  $\rightarrow$ .
  - c. acetone + phosphorus pentachloride  $\rightarrow$ .
  - d. acetone + hydrogen  $\rightarrow$ .
4. How does the structure of acetone differ from that of acetaldehyde?
5. Two isomeric compounds have the molecular formula  $C_3H_8O$ . When reduced with hydrogen, No. 1 yields normal propyl alcohol, while No. 2 gives isopropyl alcohol. Write the structural formulas of these isomers and their reactions when reduced with hydrogen.
6. Three isomeric compounds have the molecular formula  $C_3H_6O$ . No. 1 treated with hydrogen iodide yields methyl iodide, ethyl iodide, and water. When oxidized, No. 2 yields propyl aldehyde, while No. 3 gives acetone. Write the structural formulas of these compounds and verify your conclusions with equations.
7. Write the formula of an aldoxime and a ketoxime.
8. In what respects do the ketones resemble the aldehydes in their general chemical behavior, and in what respects are they different?
9. What is meant by a "mixed ketone"?
10. How could you prepare ethyl methyl ketone?

# CHAPTER SEVEN

## MONOBASIC ACIDS

Monobasic acids are compounds containing the carboxyl

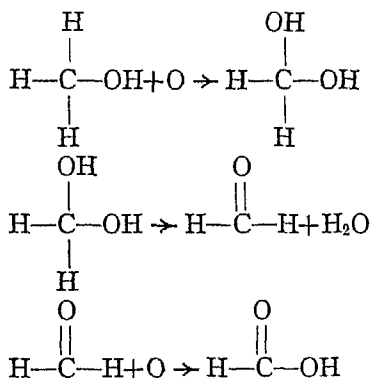
group  $\begin{array}{c} \text{O} \\ || \\ \text{C}-\text{OH, or COOH} \end{array}$ . They are regarded as derived from the hydrocarbons by the substitution of the carboxyl group for one atom of hydrogen. The following table contains the complete and the abbreviated structural formulas of a few of these compounds and the corresponding hydrocarbons from which they are derived :

MONOBASIC ACIDS

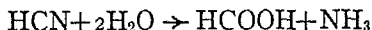
HYDROCARBONS	ACIDS	STRUCTURAL FORMULA		BOILING POINT, °C.
		Complete	Abbreviated	
	Formic	$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{OH} \end{array}$	HCOOH	101
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \\ \text{methane} \end{array}$	Acetic	$\begin{array}{c} \text{H} \quad \text{O} \\   \quad    \\ \text{H}-\text{C}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	CH <sub>3</sub> COOH	119
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \\ \text{ethane} \end{array}$	Propionic	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad    \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{OH} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	CH <sub>3</sub> CH <sub>2</sub> COOH	141
$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{propane} \end{array}$	Butyric (normal)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad   \quad    \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH	163
	Butyric (iso)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{C}=\text{O} \\ \quad \quad \quad   \\ \quad \quad \quad \text{OH} \end{array}$	(CH <sub>3</sub> ) <sub>2</sub> CHCOOH	155

These acids form a homologous series of compounds, and are called *fatty acids*, because many of the higher members occur in natural fats combined with other substances.

**Formic acid**,  $\text{HCOOH}$ , is the first member of this series. It is not derived from any hydrocarbon, but since it has the structure of these compounds it is conveniently included in this series. Formic acid occurs in plants and in certain insects, such as red ants, from which it may be obtained by distillation. It may be prepared in the laboratory by the oxidation of methyl alcohol :



Formic acid may also be obtained by the hydrolysis of hydrogen cyanide,

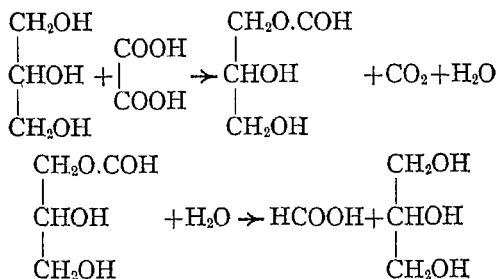


The usual laboratory method of preparation consists in distilling

a mixture of glycerol,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , and oxalic acid,  $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$ . In this

reaction glycerol monoformin,  $\begin{array}{c} \text{CH}_2\text{O.COH} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , is formed as an intermediate product which is decomposed, yielding formic acid.

## EXPERIMENT 23

Preparation of formic acid,  $\text{HCOOH}$ 

*Materials*  $\left\{ \begin{array}{l} 32 \text{ cc. dehydrated glycerol} \\ 70 \text{ grams crystallized oxalic acid} \end{array} \right.$

*Procedure.* If the glycerol is not anhydrous, it should be dehydrated in accordance with the directions given in the note at the end of this experiment. Pour 32 cc. of dehydrated glycerol into a dry 200 cc. distilling flask. Add 40 grams of crystallized oxalic acid, and stir the mixture by shaking. A cork stopper through which passes a thermometer is inserted in the top of the flask and the thermometer so adjusted that the mercury bulb dips into the glycerol. The flask is connected to a condenser and heated gradually. The reaction begins at about  $80^\circ$ , and at  $90^\circ$  carbon dioxide is evolved readily. The mixture is heated until the thermometer shows a temperature of about  $110^\circ$ , and is maintained at a temperature of  $110^\circ$  to  $120^\circ$  until the evolution of gas has slackened. The distillate consists mostly of dilute formic acid.

The flask is allowed to cool somewhat, and a second portion of oxalic acid (about 30 grams) is now added. The distillation is continued as before.

The total distillate is now poured into a dry 200 cc. distilling flask and redistilled. Collect the fraction boiling between  $90^\circ$  and  $108^\circ$ .

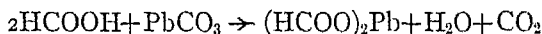
By continuing the distillation with the addition of several more portions of oxalic acid, the concentration of formic acid in the distillate is increased until the distillate contains about 56 per cent of formic acid. The boiling point of pure formic acid is  $101^\circ$ . Preserve a specimen.

*NOTE.* Anhydrous glycerol is obtained by heating glycerol to a temperature of  $175^\circ$ . The glycerol is heated in an evaporating dish, and the temperature is

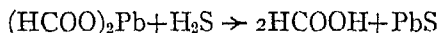


determined by inserting a thermometer into the liquid. The dehydrated glycerol is poured into a bottle, which is stoppered carefully.

Pure anhydrous formic acid may be prepared from lead formate,  $(\text{HCOO})_2\text{Pb}$ , which is obtained by treating dilute formic acid with lead carbonate:



Lead formate is converted into anhydrous formic acid by treating it with hydrogen sulfide:

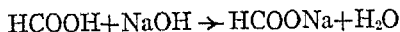


Formic acid is a colorless liquid which has a specific gravity of 1.241 at  $0^\circ$ . It has an irritating odor and produces blisters when brought into contact with the skin. It is one of the strongest organic acids and decomposes carbonates and certain metallic oxides. A solution of formic acid is easily oxidized by various substances, and the acid is therefore a good reducing agent. It precipitates silver from a neutral solution of a silver salt and reduces mercuric chloride to calomel. Formic acid gives characteristic reactions when treated with various reagents.

#### EXPERIMENT 24

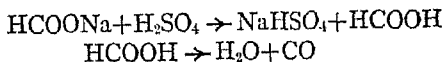
##### Reactions of formic acid, $\text{HCOOH}$

*A.* Sodium formate,  $\text{HCOONa}$ . Pour 10 cc. of formic acid into an evaporating dish. Make it exactly neutral with a dilute solution of sodium hydroxide (use litmus paper as an indicator). Evaporate nearly to dryness and allow the sodium formate to crystallize. Filter, and dry the crystals on filter paper. Preserve a specimen.

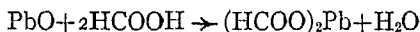


How could you prepare the barium salt of formic acid?

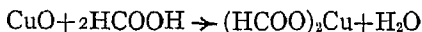
*B.* Heat in a test tube about a gram of sodium formate with about 0.5 cc. of sulfuric acid. Does the gas which is formed burn?



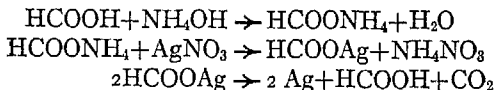
C. **Lead formate**,  $(\text{HCOO})_2\text{Pb}$ . Place about 2 grams of lead monoxide (litharge),  $\text{PbO}$ , in an evaporating dish. Add to it about 15 cc. of formic acid. Heat gently until most of the lead oxide is dissolved, and filter. Allow the filtrate to crystallize. Filter off the crystals of lead formate, and dry on filter paper. Preserve a specimen.



D. **Copper formate**,  $(\text{HCOO})_2\text{Cu}$ . Heat in an evaporating dish 2 grams of powdered cupric oxide with about 15 cc. of formic acid. When most of the oxide has dissolved, filter, and allow the filtrate to crystallize. The crystals of copper formate are filtered off and dried on filter paper. Preserve a specimen.



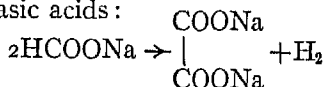
E. Neutralize in a test tube about 2 cc. of a dilute solution of formic acid (1 : 5) with a dilute solution of ammonia (1 : 5). Add about 0.5 cc. of dilute silver nitrate solution (1 : 10), and warm. Metallic silver is precipitated as a black powder:



F. Pour about 3 cc. formic acid into a test tube and add 2 cc. of mercuric chloride solution (1 : 10). When the mixture is warmed, the mercuric chloride is reduced to mercurous chloride, which is precipitated.

When sodium formate is heated to a temperature of about  $250^\circ$ , it is converted to sodium oxalate,  $\begin{array}{c} \text{COONa} \\ | \\ \text{COONa} \end{array}$ . By this re-

action it is possible to pass from the series of monobasic acids to the series of dibasic acids:

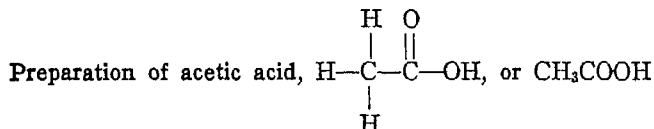


Sodium oxalate is the sodium salt of the simplest dibasic acid,

oxalic acid,  $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$ . A dibasic acid is one which contains two carboxyl groups.

**Acetic acid**,  $\text{CH}_3\text{COOH}$ , is the second member of this series of acids. The reactions of acetic acid illustrate in a general manner the chemistry of this group of compounds. It occurs naturally in many plants in combination with alcohols and is obtained by the destructive distillation of wood. When dilute solutions of alcohol, such as beer or weak wines, are exposed to the air, the alcohol is oxidized to acetic acid. The change is brought about by a process of fermentation which is caused by a living ferment called *Mycoderma aceti*. Ordinary *vinegar* is simply a dilute solution of acetic acid which contains coloring matter and other impurities. It is produced by the fermentation of weak wines or other dilute alcoholic solutions. Various methods may be used for the laboratory preparation of acetic acid. It is obtained conveniently by the interaction of sodium acetate,  $\text{CH}_3\text{COONa}$ , and sulfuric acid.

## EXPERIMENT 25

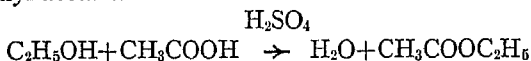


*Materials*  $\left\{ \begin{array}{l} 30 \text{ grams fused sodium acetate} \\ 18 \text{ cc. concentrated sulfuric acid} \end{array} \right.$

*Procedure.* Powder 30 grams of fused sodium acetate, and pour into a 150 cc. dry distilling flask. The fused anhydrous sodium acetate should be powdered rapidly and placed immediately in the distilling flask, as it absorbs moisture from the atmosphere. Add to this 18 cc. of concentrated sulfuric acid. Connect the flask to a condenser, place a cork stopper in the top of the distilling flask, and heat the mixture over a wire gauze. Allow the mixture to distil gradually. The distillate is poured into a 100 cc. dry distilling flask. A thermometer is placed in the top of the flask and so adjusted that the mercury bulb is level with the exit tube of the flask. Distil the acid through a condenser and observe the boiling point. The boiling

point of pure acetic acid is  $119^{\circ}$ . Weigh the product you have obtained and calculate the percentage yield. Preserve a specimen.

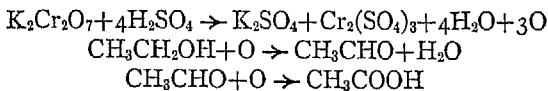
A. **Test for acetic acid.** Pour into a test tube 1 cc. of each of the following substances: glacial acetic acid, ethyl alcohol, and concentrated sulfuric acid. Warm the mixture gently and note the fruity odor of ethyl acetate.



Pure acetic acid is known as *glacial acetic*. It is a crystalline substance which melts at  $16.7^{\circ}$ . At ordinary room temperatures it is a liquid which has an odor somewhat like that of vinegar. It is soluble in water, alcohol, and ether and is used as a solvent for many organic compounds. It has a penetrating odor and when brought into contact with the skin produces blisters. It is prepared on a large scale for use in the manufacture of dyes, and of salts, such as the acetates of lead and chromium, which are of considerable practical value. Acetic acid may also be prepared by the oxidation of ethyl alcohol. In this method of preparation the intermediate product, acetaldehyde, is obtained, and this on further oxidation is converted into acetic acid.

## EXPERIMENT 26

### Preparation of acetic acid by the oxidation of ethyl alcohol

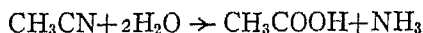


Materials	{	10 grams powdered potassium dichromate
		Solution of 10 cc. concentrated sulfuric acid dissolved
		in 20 cc. water
		Solution of 5 cc. ethyl alcohol (95 per cent) dissolved in
		15 cc. water
		Bath of ice water

**Procedure.** Powder 10 grams of potassium dichromate in a mortar and place in a 200 cc. round flask. Pour 20 cc. of water into a 100 cc. flask and hold the flask under running tap water, while 10 cc. of con-

centrated sulfuric acid are added gradually, with constant shaking and cooling. When this solution has been prepared and cooled to the room temperature, pour it into the flask containing the powdered dichromate. Connect the flask containing the mixture to a reflux condenser. Pour 15 cc. of water into a 100 cc. dropping funnel, and add 5 cc. of ethyl alcohol (95 per cent). Shake to obtain a uniform solution, and place the funnel loosely in the top of the condenser. Allow the alcohol solution to drop slowly into the dichromate solution. When all of it has been added, the flask is warmed slightly until bubbles of gas are evolved. The flame is then removed. If the action becomes too violent, the flask should be cooled temporarily by placing a bath of ice water under it, after which it should be warmed again. The liquid should boil energetically for a few minutes until the first action is over. It is then warmed with a Bunsen burner and the temperature increased until the liquid boils gently. Allow the mixture to boil about 15 minutes. The apparatus is now disconnected. The reaction product is poured into a 200 cc. distilling flask. Connect the flask to a condenser in the usual manner, and heat over a wire gauze. When about 15 cc. of the distillate, which is an aqueous solution of acetic acid, has been collected, discontinue the operation. Test with litmus to ascertain if the product has an acid reaction. Pour 10 cc. of the distillate into an evaporating dish. Neutralize carefully with a dilute sodium hydroxide solution, and evaporate to dryness on a water bath. What is the product? Test it (Experiment 25 A).

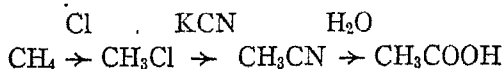
Acetic acid may be obtained by the hydrolysis of methyl cyanide,  $\text{CH}_3\text{CN}$ :



Methyl cyanide is formed by the interaction of methyl chloride and potassium cyanide:



Since methyl chloride can be prepared from methane, it is evident that it is possible to prepare acetic acid from methane by a series of reactions:



By a similar series of reactions it would be possible to prepare propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , from ethane. Write the reactions with balanced equations.

*Structure.* The structural formula  $\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$ , which has

been assigned to acetic acid, represents in a satisfactory manner the behavior of this compound. It shows that acetic acid contains the carbonyl group ( $\text{C}=\text{O}$ ) united to a methyl group and one hydroxyl radical. If acetic acid really contains these groups, it should give reactions which are characteristic of them. When methyl alcohol which contains one hydroxyl group is treated with sodium, one hydrogen atom is replaced by one atom of sodium:



Acetic acid when treated with sodium reacts in a similar manner,

forming sodium acetate,  $\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}-\text{C}-\text{C}-\text{ONa} \\ | \\ \text{H} \end{array}$ :

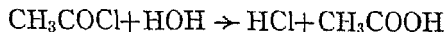


This reaction shows that one hydrogen atom in acetic acid must be situated in the molecule in a manner different from the other hydrogen atoms. By treating methyl alcohol with phosphorus pentachloride, the hydroxyl group is replaced by chlorine, forming methyl chloride. Write the equation. Acetic acid reacts in a similar manner with phosphorus pentachloride, giving acetyl

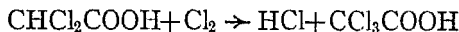
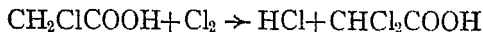
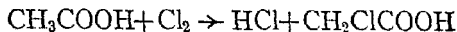
chloride,  $\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}-\text{C}-\text{C}-\text{Cl} \\ | \\ \text{H} \end{array}$ :



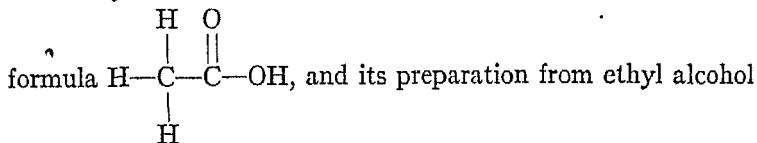
When water is added to acetyl chloride, the chlorine is replaced by the hydroxyl group :



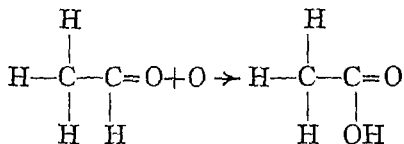
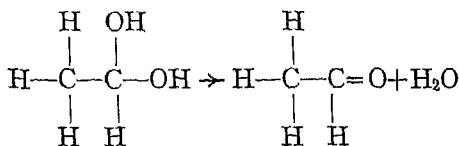
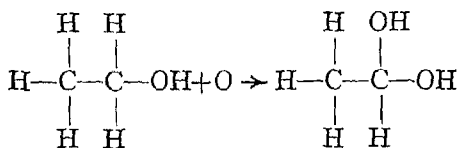
These reactions show that acetic acid contains a hydroxyl group. When acetic acid is treated with chlorine, three hydrogen atoms are replaced by chlorine. The reaction takes place in three stages :



The compound  $\text{CH}_2\text{ClCOOH}$  is called *monochlor acetic acid*.  $\text{CHCl}_2\text{COOH}$  is dichlor acetic acid, and  $\text{CCl}_3\text{COOH}$ , trichlor acetic acid. When acetic acid is treated with bromine, similar products are obtained. Write the equations. These substances are known as *substituted acetic acids*, and the substitution reactions by which they are formed are similar to those which take place when methane is treated with chlorine, since by the continued action of chlorine on methane the hydrogen atoms are gradually replaced by chlorine. We have shown, then, that acetic acid contains one hydrogen atom which is replaced by monovalent elements such as sodium, that it has a hydroxyl group replaceable by chlorine, and three hydrogen atoms which may be substituted by chlorine. These reactions indicate that acetic acid contains the methyl and hydroxyl radicals which are united to the carbonyl group ( $\text{C}=\text{O}$ ). These facts considered in connection with the manner in which acetic acid is prepared from ethyl alcohol indicate that acetic acid has the structural

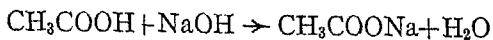


may be represented by the following reactions :



$\begin{array}{c} \text{O} \\ || \\ \text{C}-\text{OH} \end{array}$ , or  $\text{COOH}$ , is called the *carboxyl group* and is characteristic of acids such as formic and acetic. Acetic acid may be regarded, then, as derived from methane. By substituting the carboxyl group for one of the methane hydrogen atoms, we should have the compound  $\text{CH}_3\text{COOH}$ , which is acetic acid. It consists, then, of a methyl radical united to a carboxyl group.

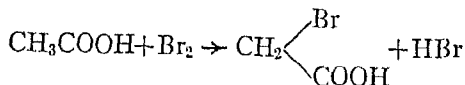
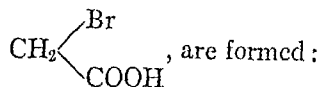
**Acid derivatives and substituted acids.** When acetic acid reacts with other substances and substitution takes place in the carboxyl part of the compound, products known as *derivatives of acetic acid* are obtained. Thus, when a given quantity of acetic acid is neutralized with a sodium hydroxide solution and the mixture evaporated to dryness, the sodium salt of acetic acid or sodium acetate,  $\text{CH}_3\text{COONa}$ , is obtained. This substance is a derivative of acetic acid:



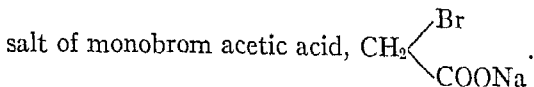
When one or more of the hydrogen atoms in the methyl radical of acetic acid are replaced by elements such as chlorine or bro-



mine, substituted acetic acids such as monobrom acetic acid,



Substituted acetic acids also yield derivatives such as the sodium



**Salts of acetic acid.** Salts of acetic acid have been known for many years, and a number of them are used extensively.

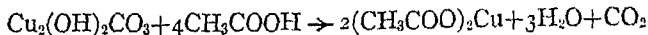
#### EXPERIMENT 27

##### Preparation of salts of acetic acid

**A. Silver acetate,  $\text{CH}_3\text{COOAg}$ .** Prepare a concentrated solution of sodium acetate by treating about 4 grams of the salt with a sufficient amount of water to dissolve it. Add to this solution about 2 cc. of a dilute solution of silver nitrate (1:10). The difficultly soluble silver acetate is precipitated:

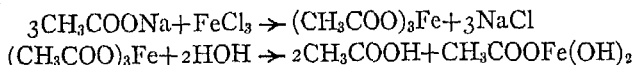


**B. Copper acetate,  $(\text{CH}_3\text{COO})_2\text{Cu}$ .** Place about 2 grams of basic copper carbonate in an evaporating dish, and add to it about 10 cc. of glacial acetic acid. Warm the mixture until the reaction, which is at first somewhat energetic, appears to be complete. Now add about 15 cc. of water and 5 cc. of acetic acid, and boil a few minutes until most of the material is dissolved. Filter into a 100 cc. beaker, and evaporate the filtrate over a wire gauze until the solution appears to be slightly supersaturated. How can you tell when this stage is reached? Set aside and allow to crystallize. Copper acetate crystallizes with two molecules of water of crystallization. Preserve a specimen.



**C. Basic ferric acetate,  $\text{CH}_3\text{COOFe}(\text{OH})_2$ .** Pour about 2 cc. of a concentrated solution of sodium acetate into a test tube, and add

about 2 cc. of ferric chloride solution (1:10). A deep-red colored solution is obtained, and when this is boiled basic ferric acetate is precipitated:



Aluminium chloride when treated with sodium acetate also gives a basic acetate precipitate. The basic acetate method used for the quantitative separation of iron and aluminium from manganese, nickel, cobalt, and zinc is based upon the reactions above.

**Lead acetate**,  $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ , is prepared by dissolving litharge,  $\text{PbO}$ , in acetic acid. It has a somewhat sweet taste and hence is called *sugar of lead*. It is very poisonous. When acetic acid is treated with an excess of litharge, basic lead acetate,

$\text{Pb} \begin{cases} \text{OH} \\ \text{OOC} \cdot \text{CH}_3 \end{cases}$ , is obtained. It is used as a clarifying reagent in sugar analysis.

**Paris green** is a double salt of copper acetate and copper arsenite. It is used to exterminate insects which are found on potato vines. The acetates of aluminium, iron, and chromium are used as mordants in dyeing.

**Propionic acid**,  $\text{C}_2\text{H}_5\text{COOH}$ , is the third member of this series of acids. It is a liquid which boils at  $141^\circ$ . It is the monocarboxyl derivative of ethane. Since all the hydrogen atoms in ethane bear the same relation to one molecule, only one propionic acid is possible. It yields a number of derivatives corresponding to those obtained from acetic acid. For instance, it forms salts, such as sodium propionate,  $\text{C}_2\text{H}_5\text{COONa}$ , similar to sodium acetate.

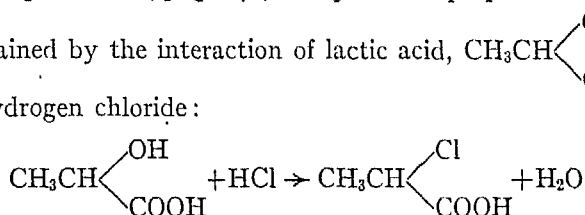
**Substituted propionic acids.** Substitution in the ethyl group of propionic acid yields compounds similar to the dichloroethanes. As we have previously stated, the formula of ethylene dichloride,  $\text{CH}_2\text{Cl}$   
 $\begin{array}{c} | \\ \text{CH}_2\text{Cl} \end{array}$ , represents the two chlorine atoms as being united to dif-

ferent carbon atoms, while in ethylidene chloride,  $\begin{array}{c} \text{CH}(\text{Cl})_2 \\ | \\ \text{CH}_3 \end{array}$ ,

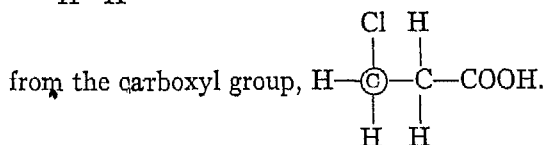
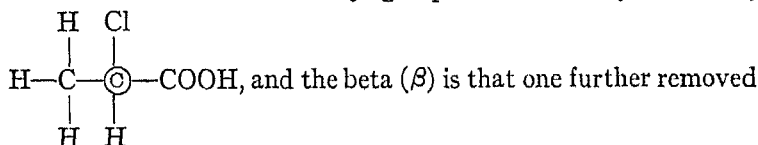
the two atoms of chlorine are represented as being united to the same carbon atom. The monochlor propionic acids have a similar constitution. In beta chlor propionic acid,  $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{Cl} \end{array}$ , or

$\text{CH}_2\text{ClCH}_2\text{COOH}$ , the one atom of chlorine and the carboxyl group are united to different carbon atoms. This compound may be prepared from ethylene by a series of reactions (see Beta chlor propionic acid, page 171). Alpha chlor propionic acid may

be obtained by the interaction of lactic acid,  $\text{CH}_3\text{CH} \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{COOH} \end{array}$ , and hydrogen chloride:



The monochlor substitution products of propionic acid exist, then, in isomeric forms. In order to distinguish these isomers, we assign a name to the carbon atom of the group in which substitution has taken place. The alpha carbon atom ( $\alpha$ ) is that which is united to the carboxyl group as indicated by the circle,



**Butyric acids,  $\text{C}_4\text{H}_8\text{O}_2$ .** Since propane contains two different sets of hydrogen atoms, it therefore yields two isomeric mono-

carboxyl derivatives. One of these, normal butyric acid,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ , or  $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ , is found in rancid butter, while the other, which is isobutyric acid,  $(\text{CH}_3)_2\text{CHCOOH}$ , occurs in aconite root and other substances.

*Nomenclature.* In naming the monobasic acids, it is customary to consider them as derived from acetic acid, just as the alcohols are regarded as derived from methyl alcohol. Thus propionic

acid,  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2\text{COOH} \end{array}$ , is called *methyl acetic acid*, and normal butyric

acid,  $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{CH}_2\text{COOH} \end{array}$ , is *ethyl acetic acid*.

**Valeric acids**,  $\text{C}_5\text{H}_{10}\text{O}_2$ . There are two butanes, and each of these yields by substitution two monocarboxyl derivatives. Propyl acetic acid, (normal valeric acid)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ,

or  $\text{CH}_2 \begin{array}{l} \nearrow \text{CH}_2\text{CH}_2\text{CH}_3 \\ \searrow \text{COOH} \end{array}$ , and ethyl methyl acetic acid,

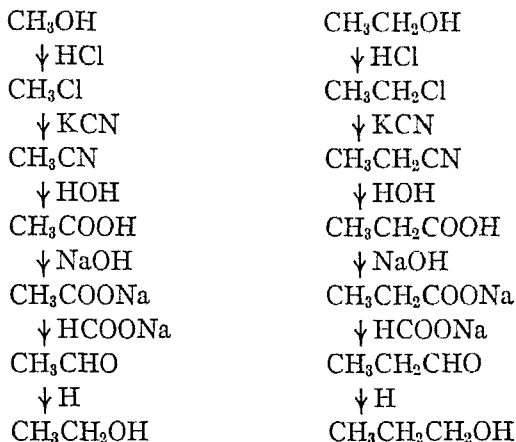
$\text{CH}_3\text{CH}_2\text{CH} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{COOH} \end{array}$ , or  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}_2\text{H}_5 \end{array} \begin{array}{l} \nearrow \\ \searrow \end{array} \text{CHCOOH}$ , are derivatives of nor-

mal butane. Isopropyl acetic acid,  $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$ , and trimethyl acetic acid,  $\text{C}(\text{CH}_3)_3\text{COOH}$ , are derived from isobutane. These four valeric acids, as indicated by their names, are distinguished by regarding them as substituted acetic acids.

**Palmitic acid**,  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ , and **stearic acid**,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , which are higher members of this series, occur in large quantities in animal and vegetable fats. The sodium and potassium salts of these acids are the principal constituents of soaps.

**Synthetic relations.** We have shown how it is possible to prepare a higher member of the paraffin hydrocarbons such as propane from a lower member like methane (see Synthetic chemistry, page 33). In studying the methods of preparation and

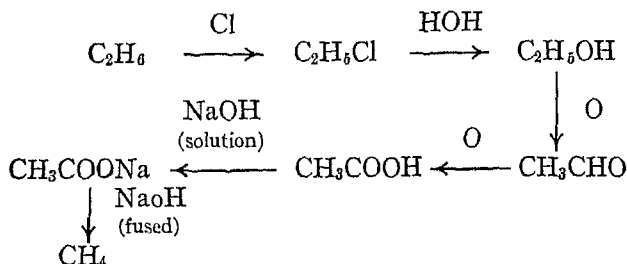
characteristic reactions of such compounds as alcohols, aldehydes, and acids, we have become familiar with a number of reactions, a few of which may be used synthetically. The following series of outline reactions show how it is possible to build up in the laboratory a higher alcohol from a lower one :



As shown by the outline reactions above, methyl alcohol may be converted to methyl chloride, which reacts with potassium cyanide, forming methyl cyanide. This compound when hydrolyzed yields acetic acid, which when neutralized with sodium hydroxide gives sodium acetate. The latter reacts with sodium formate, yielding acetaldehyde, which when reduced gives ethyl alcohol. By continuing this synthetic process ethyl alcohol may be converted by a similar series of reactions into propyl alcohol. Thus by this synthetical process we are able to prepare a higher alcohol from a lower one and also, from the corresponding lower intermediate products, all the higher intermediate products, such as chlorides, cyanides, acids, salts, and aldehydes.

Not only is it possible to build up complex compounds from simple ones, but the higher compounds may also be converted

into simpler ones with the separation of intermediate products. This is shown in the following series of reactions :



These reactions show that it is possible to prepare methane from ethane with the separation of various intermediate products.

Methods of synthetic organic chemistry have enabled us to prepare many new compounds having valuable properties. Indigo, a natural dye, obtained from the indigo plant, is used in enormous quantities for dyeing various materials. Some years ago large tracts of land were used for growing the indigo plant. Researches carried out by certain chemists showed that indigo could be made in the laboratory cheaper than it could be grown, and as a result it is now prepared synthetically and the land and labor formerly devoted to the cultivation of indigo may be used for other purposes. Many valuable medicinal remedies are obtained from plants. By investigating these natural substances and studying their chemical behavior, chemists have been able to prepare synthetically new compounds of similar structure and to study the relative medicinal value of the synthetic and natural products. The result is that a number of new compounds have been discovered having valuable medicinal properties.

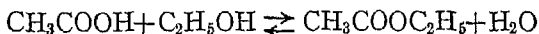
## QUESTIONS

1. What kind of compounds are monobasic acids?
2. Write equations showing how formic acid may be obtained from methyl alcohol and from hydrogen cyanide.
3. Explain, with equations, the laboratory preparation of salts of formic acid, such as the sodium, barium, lead, and copper salts.
4. Explain, with equations, the laboratory preparation of acetic acid from sodium acetate and from ethyl alcohol.
5. How do you test for acetic acid and acetates?
6. Write outline equations showing how acetic acid could be prepared from methane.
7. Explain, with equations, how the structural formula of acetic acid is determined.
8. Explain, with examples, what is meant by "acid derivatives" and "substituted acids."
9. How are the copper and sodium salts of acetic acid prepared?
10. Write the complete structural formulas of the following acids: methyl acetic acid; propyl acetic acid; trimethyl acetic acid.
11. Write outline equations:
  - a. methyl alcohol  $\rightarrow$  ethyl alcohol.
  - b. ethyl chloride  $\rightarrow$  methyl chloride.
12. Explain the value of methods of synthetic chemistry.
13. Explain, with equations, the laboratory preparation of propionic acid.
14. How could you prepare the barium salt of propionic acid?

## CHAPTER EIGHT

### ESTERS

**Esters** of the monobasic acids are formed by replacing the hydrogen atom of the carboxyl group (COOH) by an alkyl radical. Thus, if the carboxyl hydrogen atom of acetic acid,  $\text{CH}_3\text{COOH}$ , is replaced by the ethyl radical, the ethyl ester of acetic acid or *ethyl acetate*,  $\text{CH}_3\text{COOC}_2\text{H}_5$ , is obtained. Esters of organic acids are usually prepared by the interaction of organic acids and alcohols. Thus, ethyl acetate is obtained by treating ethyl alcohol with acetic acid:



The reaction is reversible, and in order to prevent the reverse action and obtain a large yield of ester it is necessary to use a dehydrating agent to absorb the water formed in the forward action. In this case sulfuric acid is used.

Another method of preventing the reverse action is to use substances which will cause a precipitate to be formed as a result of the forward action. This may be accomplished by allowing the silver salt of an acid to react with an alkyl halide:

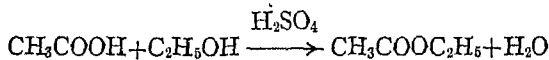
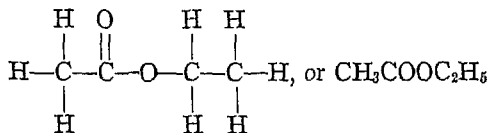


In this case the insoluble silver bromide is precipitated and thus eliminated from the field of action, and consequently the reaction is not reversible.

Esters may also be prepared by treating alcohols with acid chlorides or anhydrides. These reactions will be considered later.

### EXPERIMENT 28

#### Preparation of ethyl acetate

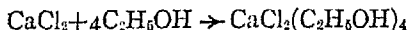




<i>Materials</i>	{	40 cc. concentrated sulfuric acid
		40 cc. absolute alcohol
		40 cc. glacial acetic acid
		40 cc. absolute alcohol
		Solution of 5 grams of sodium carbonate dissolved in 30 cc. of water
		Solution of 25 grams of calcium chloride dissolved in 25 cc. of water
		Anhydrous calcium chloride
		Oil bath

*Procedure.* Pour 40 cc. of absolute alcohol into a dry 300 cc. distilling flask, and add, with constant shaking and cooling, 40 cc. of concentrated sulfuric acid. The flask is provided with a cork stopper having one hole, through which a dropping funnel passes. The flask is connected to a condenser. 40 cc. of absolute alcohol are added to 40 cc. of glacial acetic acid and the mixture poured into the dropping funnel. An oil bath is now placed under the flask in such a position that the flask is partly immersed in the oil. A thermometer is attached to the iron stand and allowed to dip below the surface of the oil. The oil bath is now heated gradually. As soon as the reaction begins, which is usually at about  $165^{\circ}$ , the mixture begins to boil and distils over into the receiver. The flame is now removed and the bath allowed to cool to  $140^{\circ}$ , at which temperature it is maintained during the experiment. The mixture of acetic acid and alcohol is allowed to drop slowly into the flask at about the same rate as the ester distils over. The distillate contains in addition to ethyl acetate small amounts of acetic acid and alcohol, which also distil over. It is also contaminated with a small amount of ether and sulfuric acid.

The ester is purified in the following manner: The distillate is poured into a separating funnel, and to it is added a solution consisting of 5 grams of sodium carbonate dissolved in 30 cc. of water to neutralize the acids. Shake, and remove the lower layer of carbonate solution. Now add a solution consisting of 25 grams of calcium chloride, dissolved in 25 cc. of water, to remove the alcohol which has distilled over with the ethyl acetate during the experiment. The calcium chloride unites with the alcohol, forming a double compound:



The lower layer of chloride solution is now separated, and the ethyl acetate is poured from the mouth of the funnel into an Erlenmeyer flask. Add about eight pieces (pea size) of granulated calcium chloride to absorb the small amount of water which the ester contains. The flask is now firmly stoppered and set aside for several hours.

When the ester is completely dehydrated, as shown by the fact that it presents a clear and not a milky appearance, it is filtered into a 200 cc. distilling flask and distilled over a water bath, with a thermometer inserted in the neck of the distilling flask. Should the bulb of the thermometer dip into the liquid, or should it be placed at the exit tube? Explain. Collect the fraction boiling between  $74^{\circ}$  and  $79^{\circ}$ . The yield is usually about 80 per cent of the theory. Weigh the quantity of ester obtained and calculate the yield. The boiling point of ethyl acetate is  $77^{\circ}$ . It is soluble in alcohol, ether, and acetic acid. Calculate the yield and preserve a specimen.

NOTE. If an oil bath is not available, the exact temperature of the experiment may also be obtained by inserting a thermometer into the reacting mixture as in the preparation of formic acid (Experiment 23).

Esters are usually colorless liquids which have a very agreeable odor, and many of them have a very pleasant taste. Many esters occur naturally in fruits and flowers, and the pleasant odors of these are frequently due to the esters they contain. A number of esters are manufactured commercially and employed in the preparation of fruit essences and perfumes. Ethyl butyrate has a pleasant odor resembling that of pineapples, and the odor of amyl acetate is like that of pears. Esters form many isomeric compounds. For example, ethyl formate,  $\text{HCOOC}_2\text{H}_5$ , methyl acetate,  $\text{CH}_3\text{COOCH}_3$ , and propionic acid,  $\text{C}_2\text{H}_5\text{COOH}$ , are isomers. In the tables on pages 135 and 136 are given a few of the simpler esters of acetic acid and the ethyl esters of a few monobasic acids.

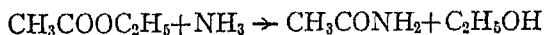
In general these esters may be prepared by methods similar to those used in making ethyl acetate. They are usually prepared by the interaction of the proper acids and alcohols in the presence of a suitable dehydrating agent. A general formula

## ESTERS OF ACETIC ACID

NAME	STRUCTURAL FORMULA		BOILING POINT, °C.
	Complete	Abbreviated	
Methyl acetate	$  \begin{array}{c}  \text{H} \quad \text{O} \quad \text{H} \\    \quad    \quad   \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\    \quad \quad   \\  \text{H} \quad \quad \text{H}  \end{array}  $	$\text{CH}_3\text{COOCH}_3$	57.5
Ethyl acetate	$  \begin{array}{c}  \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\    \quad    \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\    \quad \quad   \quad   \\  \text{H} \quad \quad \text{H} \quad \text{H}  \end{array}  $	$\text{CH}_3\text{COOC}_2\text{H}_5$	77
Propyl acetate	$  \begin{array}{c}  \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \\    \quad    \quad   \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{C}-\text{H} \\    \quad \quad   \quad   \quad   \\  \text{H} \quad \quad \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$	101
Propyl acetate (iso)	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\text{H} \\    \\  \text{H} \quad \text{O} \\    \quad    \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\    \quad \quad   \\  \text{H} \quad \quad \text{H}-\text{C}-\text{H} \\  \quad \quad   \\  \quad \quad \text{H}  \end{array}  $	$\text{CH}_3\text{COOCH}(\text{CH}_3)_2$	91

for esters of the monobasic acids is  $\text{RCOOR}'$ , where R and R' represent the same or different radicals.

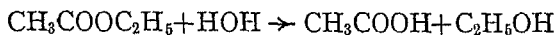
When treated with concentrated ammonia, esters yield amides. Thus, acetamide,  $\text{CH}_3\text{CONH}_2$ , may be prepared by the interaction of ethyl acetate and ammonia (see Experiment 32, page 147):



## ETHYL ESTERS OF MONOBASIC ACIDS

NAME	STRUCTURAL FORMULA		BOILING POINT, °C.
	Complete	Abbreviated	
Ethyl formate	$  \begin{array}{c}  \text{O} \quad \text{H} \quad \text{H} \\  \parallel \quad   \quad   \\  \text{H}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\  \quad \quad   \quad   \\  \quad \quad \text{H} \quad \text{H}  \end{array}  $	$\text{HCOOC}_2\text{H}_5$	55
Ethyl acetate	$  \begin{array}{c}  \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\    \quad \parallel \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\    \quad \quad \quad   \quad   \\  \text{H} \quad \quad \quad \text{H} \quad \text{H}  \end{array}  $	$\text{CH}_3\text{COOC}_2\text{H}_5$	77
Ethyl propionate	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\    \quad   \quad \parallel \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\    \quad   \quad \quad \quad   \quad   \\  \text{H} \quad \text{H} \quad \quad \quad \text{H} \quad \text{H}  \end{array}  $	$\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$	98.8
Ethyl butyrate (normal)	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{H} \\    \quad   \quad   \quad \parallel \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\    \quad   \quad   \quad \quad \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H} \quad \quad \quad \text{H} \quad \text{H}  \end{array}  $	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	120.9
Ethyl butyrate (iso)	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C}-\text{H} \\    \\  \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\  \quad \parallel \quad \quad   \quad   \\  \quad \text{O} \quad \quad \text{H} \quad \text{H} \\    \quad \quad \quad   \quad   \\  \text{H}-\text{C}-\text{H} \quad \quad \text{H} \quad \text{H} \\    \\  \text{H}  \end{array}  $	$(\text{CH}_3)_2\text{CHCOOC}_2\text{H}_5$	110.1

Esters are usually hydrolyzed by water or decomposed by solutions of alkalis:



The decomposition of esters by alkalis is usually spoken of as *saponification*, since this process is employed in making soaps.

## EXPERIMENT 29

## Saponification of ethyl acetate

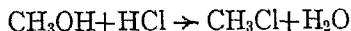


*Materials*  $\left\{ \begin{array}{l} 10 \text{ cc. ethyl acetate} \\ \text{Solution of 5 grams of sodium hydroxide dissolved in} \\ 50 \text{ cc. of water} \end{array} \right.$

*Procedure.* Pour 10 cc. of ethyl acetate into a 200 cc. round flask. Add to this a solution consisting of 5 grams of sodium hydroxide dissolved in 50 cc. of water. The flask is connected to a reflux condenser and heated on a wire gauze about 0.5 hour. The apparatus is now rearranged and the liquid distilled until about one half of it has passed over. Test for ethyl alcohol in the distillate by the iodoform reaction. (See Experiment 16 C.) The alkaline liquid remaining in the flask is poured into a 200 cc. evaporating dish; neutralize carefully the excess of sodium hydroxide present with dilute sulfuric acid (1:10) and evaporate to dryness on a water bath. Place about 0.5 gram of the dry material in a test tube; add about 1 cc. of ethyl alcohol and 0.5 cc. of concentrated sulfuric acid. Shake and warm. Do you recognize the odor of ethyl acetate? Write the equations. Could this test be used for other acetates?

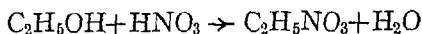
Esters are usually identified by decomposing them with an alkali solution. The resulting products, the alkali salt of the organic acid and an alcohol, are then separated and identified by special reactions.

Esters of inorganic acids may be prepared by the interaction of alcohols and inorganic acids. Thus, methyl chloride may be obtained by treating methyl alcohol with hydrogen chloride:



A compound such as methyl chloride may be considered the methyl ester of hydrogen chloride or a halogen monosubstitution

product of methane. Ethyl hydrogen sulfate,  $C_2H_5HSO_4$ , is obtained by treating ethyl alcohol with sulfuric acid (see Experiment 12). Ethyl nitrate,  $C_2H_5NO_3$ , is formed by the interaction of ethyl alcohol and nitric acid:



The reaction is unsatisfactory because a part of the nitric acid is reduced to nitrous acid. If urea is added to the mixture, the nitrous acid is decomposed and ethyl nitrate is the principal product.

### QUESTIONS

1. What kind of compounds are esters?
2. From what substance is ethyl acetate derived? How?
3. Explain, with equations, the preparation of ethyl acetate.
4. When ethyl acetate has been prepared in the crude condition, what impurities are present and how is ethyl acetate separated from these impurities?
5. Esters may be prepared by the interaction of acids and alcohols; the reactions are reversible. How is the reverse action prevented?
6. What is meant by "saponification"?
7. When ethyl acetate is saponified by a solution of potassium hydroxide, how are the products of the action separated and identified?
8. Two compounds have the molecular formula  $C_4H_8O_2$ . When hydrolyzed, No. 1 yields propionic acid and methyl alcohol, while No. 2 gives acetic acid and ethyl alcohol. Write the structural formulas of these compounds and verify your conclusion with equations.
9. Write the complete structural formulas of the following compounds: methyl propionate; propyl ester of propionic acid; ethyl butyrate (normal); methyl ester of alpha chlor propionic acid.
10. Write the following reactions in outline equations:
  - a. acetic acid  $\rightarrow$  sodium salt of monochlor acetic acid.
  - b. ethyl alcohol  $\rightarrow$  methyl ester of acetic acid.
11. Write the structural formulas of the methyl esters of the monocarboxyl derivatives of propane.
12. How are esters of inorganic acids prepared?
13. Explain with equations the preparation of the ethyl ester of propionic acid.
14. What products are obtained by saponifying ethyl propionate with potassium hydroxide? How are these products separated?

## CHAPTER NINE

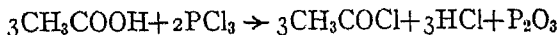
### ACID CHLORIDES, ANHYDRIDES, AND AMIDES

THE acid chlorides are derivatives of the fatty acids formed by replacing the hydroxyl group of the acid by one atom of chlorine. They are sometimes called *acyl chlorides*. When

#### ACID CHLORIDES

NAME	STRUCTURAL FORMULA		BOILING POINT, °C.
	Complete	Abbreviated	
Acetyl chloride	$  \begin{array}{c}  \text{H} \quad \text{O} \\    \quad    \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \\  \text{H}  \end{array}  $	$\text{CH}_3\text{COCl}$	55
Propionyl chloride	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{O} \\    \quad   \quad    \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $	$\text{C}_2\text{H}_5\text{COCl}$	80
Butyryl chloride (normal)	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \\    \quad   \quad   \quad    \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Cl} \\    \quad   \quad   \\  \text{H} \quad \text{H} \quad \text{H}  \end{array}  $	$\text{CH}_3(\text{CH}_2)_2\text{COCl}$	101
Butyryl chloride (iso)	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{H} \\    \quad   \quad   \\  \text{H}-\text{C}-\text{C}-\text{CH} \\    \quad   \quad   \\  \text{H} \quad \text{C}=\text{O} \quad \text{H} \\    \\  \text{Cl}  \end{array}  $	$(\text{CH}_3)_2\text{CHCOCl}$	92

acetic acid is treated with phosphorus trichloride, the hydroxyl group of the acid is replaced by chlorine:



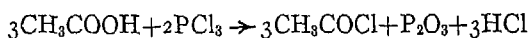
The compound  $\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}-\text{C}-\text{C}-\text{Cl} \\ | \\ \text{H} \end{array}$ , or  $\text{CH}_3\text{COCl}$ , is called *acetyl*

*chloride* because it contains the acetyl group ( $\text{CH}_3\text{CO}$ ). In the table on page 139 are given the acid chlorides of a few of the lower members of the fatty acids. The simplest member of this series would be formyl chloride,  $\text{HCOCl}$ . Attempts to make this compound have failed, as it decomposes into carbon monoxide and hydrogen chloride,  $\text{HCOCl} \rightarrow \text{CO} + \text{HCl}$ .

**Acetyl chloride**,  $\text{CH}_3\text{COCl}$ , is the first member of this series. It is prepared by the interaction of acetic acid and phosphorus trichloride.

## EXPERIMENT 30

Preparation of acetyl chloride,  $\begin{array}{c} \text{H} \quad \text{O} \\ | \quad || \\ \text{H}-\text{C}-\text{C}-\text{Cl} \\ | \\ \text{H} \end{array}$ , or  $\text{CH}_3\text{COCl}$



<i>Materials</i>	{	24 cc. glacial acetic acid
		12 cc. phosphorus trichloride
		Sodium hydroxide solution (35 grams in 200 cc. of water)
		Soda lime
		Ice water

**Procedure.** Arrange the apparatus as shown in Figure 14. A 200 cc. distilling flask, *A*, is connected to a condenser, *B*, which in turn is connected to another distilling flask, *C*. The exit end of the second distilling flask, *C*, is joined to a calcium chloride tube, *D*, which contains soda lime. A small roll of glass wool is placed at each end of the calcium chloride tube to prevent the soda lime from falling out. The chloride tube, *D*, is connected to a filtering flask, *E*, which contains a solution of sodium hydroxide prepared by dissolving 35 grams of sodium hydroxide in 200 cc. of water. Be careful that the tube which connects the calcium chloride tube, *D*, with the filtering flask



does not touch the sodium hydroxide solution. The side tube of the filtering flask is connected to another calcium chloride tube, *II*, which

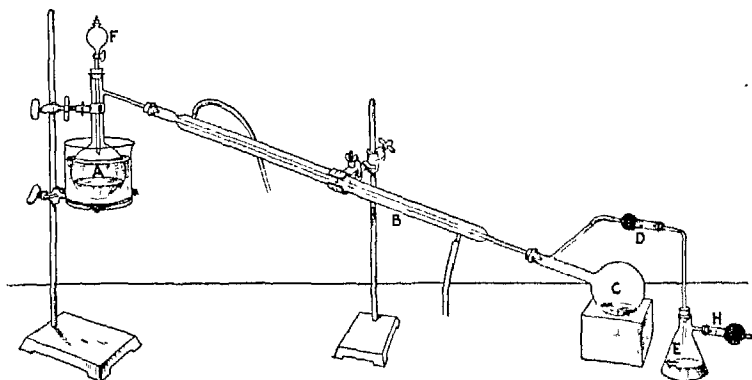


Figure 14

contains soda lime. The tube *D*, containing soda lime, absorbs a considerable portion of the hydrogen chloride gas which is given off during the reaction and also prevents moisture from entering the apparatus. The sodium hydroxide solution in the flask *E* and the soda lime in tube *H* absorb the hydrogen chloride gas which escapes from the tube *D*.

Insert into the neck of the distilling flask, *A*, a cork stopper through which passes a dropping funnel, *F*.

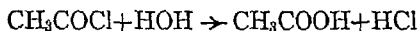
When the entire apparatus has been properly arranged, remove the dropping funnel, *F*, insert a long funnel into the neck of the distilling flask, *A*, and pour through it 24 cc. of glacial acetic acid. Remove the long funnel and again replace the dropping funnel, *F*. Close the stopcock of the dropping funnel, and pour 12 cc. of phosphorus trichloride into it. The phosphorus trichloride is allowed to drop gradually on the acetic acid. To prevent the mixture from becoming too warm, place a large beaker containing ice water under the distilling flask, *A*, so that the flask is partly immersed in the water. When all the acetyl chloride has been added to the acetic acid, the ice water in the beaker is replaced by water (at room temperature) which is gradually heated to 45°, and the temperature of this bath maintained until the active evolution of hydrogen chloride slackens. The water in the bath beneath the distilling flask is now heated until it boils, and the boiling is continued as long as the chloride distils.

The apparatus is now disconnected and the flask *C*, containing the distillate, is connected to a condenser. A thermometer is inserted into the neck of the flask and the reaction product redistilled over a water bath in the usual manner, except that the distillate is protected from atmospheric moisture by a tube containing granulated calcium chloride (see Experiment 15). Collect the fraction boiling between 52° and 58°. The boiling point of acetyl chloride is 55°. Calculate the theoretical yield. Weigh the product obtained and calculate the percentage yield. Preserve a specimen.

A. Pour 1 cc. of ethyl alcohol into a test tube, and add slowly with constant cooling 1 cc. of acetyl chloride. Now add 1 cc. of a concentrated solution of sodium chloride. Ethyl acetate, which is lighter than the salt solution, will separate out on the surface of the mixture and may be recognized by its fragrant odor:



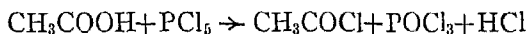
B. Add a few drops of acetyl chloride to about 5 cc. of water in a test tube. On shaking, the mixture becomes warm, and the chloride dissolves rapidly. Hydrogen chloride gas is evolved and the chloride is converted into acetic acid:



When acetyl chloride is treated with alcohol, ethyl acetate and hydrogen chloride are obtained (Experiment 30 A, above). As shown by the equation, one molecule of hydrogen chloride is obtained from one molecule of ethyl alcohol which contains one hydroxyl group. When acetyl chloride is treated with a compound which contains two hydroxyl groups, two molecules of hydrogen chloride are evolved. Thus, when a compound is treated with acetyl chloride, one molecule of hydrogen chloride is evolved for every hydroxyl group which the compound contains, and consequently acetyl chloride may be used for determining the presence and number of hydroxyl groups in a compound.

**Acetyl bromide**,  $\text{CH}_3\text{COBr}$ , may be prepared in a manner similar to that used in making acetyl chloride.

Acid chlorides may also be prepared by the interaction of monobasic acids and phosphorus pentachloride:



The lower members of this series are liquids which have a penetrating odor and fume in the air.

### QUESTIONS

1. What kind of compounds are acid chlorides?
2. From what compound is acetyl chloride derived? How?
3. How is acetyl chloride prepared?
4. What is the acetyl group?
5. When acetyl chloride is distilled, why must the distillate be protected from the atmospheric moisture? How is this accomplished?
6. Explain how acetyl chloride may be used to determine the presence and number of hydroxyl groups in a compound.
7. Write the structural formula of the acid chloride of propionic acid. How could this substance be prepared?

### ANHYDRIDES

The acid anhydrides may be considered as derived from two molecules of a monobasic acid by the removal of one molecule of water. Thus, if one molecule of water is withdrawn from two molecules of acetic acid, the resulting product is the anhydride of acetic acid, (acetic anhydride)  $(\text{CH}_3\text{CO})_2\text{O}$ . The following table contains the abbreviated structural formulas and boiling points of a few of these compounds:

#### ANHYDRIDES

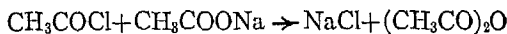
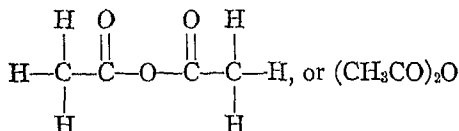
NAME	FORMULA	BOILING POINT, °C.
Acetic anhydride . . .	$(\text{CH}_3\text{CO})_2\text{O}$	136
Propionic anhydride . .	$(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$	167
Butyric anhydride (normal) . . . . .	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CO})_2\text{O}$	192
Butyric anhydride (iso)	$\left(\begin{smallmatrix} \text{CH}_3 \\   \\ \text{CH} > \text{CHCO} \end{smallmatrix}\right)_2\text{O}$	182

These compounds are usually prepared in the laboratory by the interaction of an acid chloride and the sodium salt of an acid. The simplest member of this series of compounds would be formic anhydride,  $(\text{HCO})_2\text{O}$ . This compound, however, is unstable and does not exist.

**Acetic anhydride**,  $(\text{CH}_3\text{CO})_2\text{O}$ , is the first member of this series. It is prepared conveniently by the interaction of sodium acetate and acetyl chloride.

#### EXPERIMENT 31

##### Preparation of acetic anhydride



*Materials*  $\left\{ \begin{array}{l} 33 \text{ grams of fused sodium acetate} \\ 25 \text{ cc. acetyl chloride} \end{array} \right.$

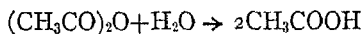
*Procedure.* Place 33 grams of powdered, fused sodium acetate in a dry 100 cc. distilling flask. A dry dropping funnel is placed in the neck of the flask, which is now immersed in ice water. Measure 25 cc. of acetyl chloride in a dry measuring cylinder and pour it into the dropping funnel. About half of the acetyl chloride is allowed to drop gradually on the sodium acetate. Remove the dropping funnel and stir the mixture by means of a thick glass rod inserted through the neck of the flask. The remainder of the chloride is now added gradually. The side tube of the flask is closed by placing a small piece of rubber tubing over the end and closing it with a pinchcock.

The flask is attached to a reflux condenser and heated on a boiling water bath about 20 minutes to complete the reaction. The apparatus is now disconnected and rearranged in the ordinary manner for distillation. A dry filtering flask which serves as a receiver for the distillate should be securely connected to the end of the condenser by means of an adapter. The side tube of the filtering flask is joined to a calcium chloride tube filled with soda lime, which serves to protect the distillate from atmospheric moisture. The neck of the distilling flask is closed by a cork stopper, and the flask is now heated

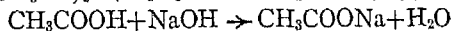
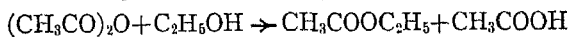
by a small flame from a Bunsen burner which is held in the hand and moved about to prevent the flask from breaking. When no more of the anhydride passes over, discontinue the operation. The reaction product is placed in a dry 100 cc. distilling flask and redistilled, a thermometer being used to indicate the boiling point and the distillate again being protected from atmospheric moisture. Collect the fraction boiling between  $130^{\circ}$  and  $140^{\circ}$ .

Pure acetic anhydride is a colorless liquid boiling at  $136^{\circ}$ . Calculate the theoretical yield. Weigh the product obtained and calculate the percentage yield. Preserve a specimen.

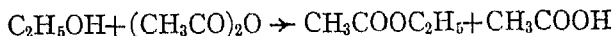
A. Add a few drops of acetic anhydride to about 5 cc. of water in a test tube, and warm. Does the product show an acid reaction?



B. Add 1 cc. of absolute ethyl alcohol to about 1 cc. of acetic anhydride in a test tube. Warm gently, and make the solution alkaline with a dilute sodium hydroxide solution (1 : 10). What odor is given off?



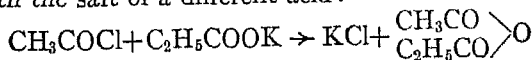
Ethyl alcohol which contains one hydroxyl group reacts with acetic anhydride to form ethyl acetate and one molecule of acetic acid :



When a compound which contains hydroxyl groups is treated with acetic anhydride, one molecule of acetic acid is formed for each hydroxyl group present in the compound. Acetic anhydride may, therefore, be used to determine the presence and number of hydroxyl groups in organic compounds.

The lower members of this series of anhydrides are liquids, while the higher members are solids. These anhydrides are usually insoluble in water but soluble in ether. When treated with water they are converted into the corresponding acids.

**Mixed anhydrides** are those which contain different alkyl radicals. They may be prepared by treating the chloride of an acid with the salt of a different acid :

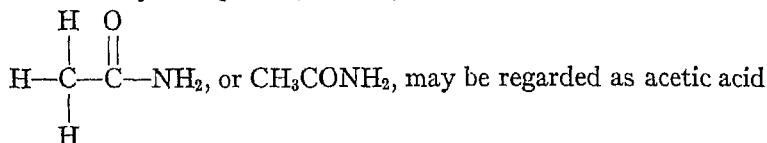


## QUESTIONS

1. What kind of compounds are the acid anhydrides?
2. Write the complete structural formula of propionic anhydride.
3. How is acetic anhydride prepared?
4. What compound would be formed by treating propionic anhydride with water?
5. How may acetic anhydride be used to determine the presence and number of hydroxyl groups in organic compounds?
6. What are mixed anhydrides and how are they prepared?
7. Write equations showing the preparation of propionic anhydride.

## AMIDES

There are three classes of acid amides: primary, secondary, and tertiary. A **primary amide**, such as acetamide,



in which the hydroxyl group has been replaced by the  $\text{NH}_2$  group which is called the amino, or amido, group. A primary amide may also be considered as derived from ammonia,  $\text{NH}_3$ , by replacing one hydrogen atom by a group such as the acetyl group ( $\text{CH}_3\text{CO}$ ):



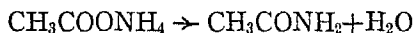
A few primary amides are given in the following table:

## AMIDES

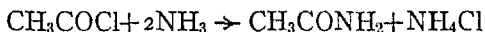
NAME	FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Formamide . . .	$\text{HCONH}_2$	Decomposes	206
Acetamide . . .	$\text{CH}_3\text{CONH}_2$	82	222
Propionamide . . .	$\text{C}_2\text{H}_5\text{CONH}_2$	79	213
Butyramide (normal)	$\text{CH}_3(\text{CH}_2)_2\text{CONH}_2$	115	216
Butyramide (iso) .	$(\text{CH}_3)_2\text{CHCONH}_2$	128	218

**Formamide**,  $\text{HCONH}_2$ , the simplest member of this series, is a liquid. The other members are crystalline solids.

**Acetamide**,  $\text{CH}_3\text{CONH}_2$ , is the second member of this series. The methods of preparation and characteristic reactions of acetamide illustrate the chemistry of this series of compounds. Like other primary amides, acetamide may be prepared by various methods. It is obtained by heating ammonium acetate:

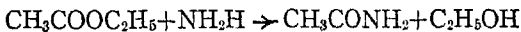
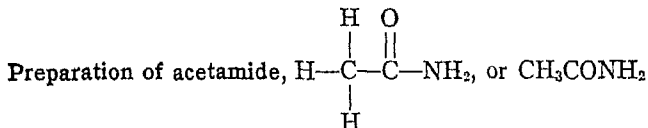


It is made also by the interaction of acetyl chloride and ammonia:



It is prepared conveniently by treating ethyl acetate with ammonia.

#### EXPERIMENT 32

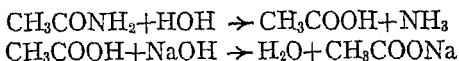


*Materials*  $\left\{ \begin{array}{l} 30 \text{ cc. ethyl acetate} \\ 30 \text{ cc. concentrated ammonia water} \end{array} \right.$

*Procedure.* Pour 30 cc. of ethyl acetate into a 100 cc. Erlenmeyer flask and add 30 cc. of concentrated ammonia. The flask should be stoppered loosely and allowed to stand about 48 hours. The mixture should be shaken occasionally; when it appears to be homogeneous, it is poured into a 100 cc. distilling flask. Place a thermometer in the neck of the flask, and distil through a condenser. Collect the first fraction of about 6 cc. and test for ethyl alcohol. When the thermometer registers a temperature of about  $170^\circ$ , the water condenser is removed and replaced by an air condenser, which is simply a long glass tube of about the same size as the inner tube of a water condenser. Should the amide crystallize out in the air condenser during the distillation, it may be liquefied by warming the condenser. When the distillate is cooled, acetamide crystallizes. Filter, and dry on layers of filter paper. Acetamide crystallizes in colorless needles

which melt at  $82^{\circ}$  and boil at  $222^{\circ}$ . It is soluble in water and alcohol. When freshly prepared it has a strong odor resembling mice, but when carefully purified it has only a slight odor. Calculate the theoretical yield and the percentage yield obtained. Preserve a specimen.

A. Boil in a test tube 0.5 gram of acetamide with about 5 cc. of a sodium hydroxide solution (1:5). The amide is hydrolyzed, giving ammonia and acetic acid, which reacts with the alkali, forming sodium acetate:



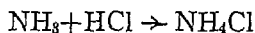
Other primary amides, such as propionamide, are prepared by methods similar to those used in making acetamide.

*Reactions of amides.* The amides are easily hydrolyzed and in this respect differ from the amines, which are compounds such as methyl amine,  $\text{CH}_3\text{NH}_2$ , containing the amino group.

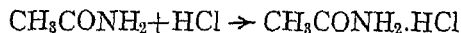
When amides are treated with nitrous acid, the amino group is replaced by hydroxyl. This reaction is characteristic of compounds containing the amino group:



Ammonia unites with hydrogen chloride, forming ammonium chloride:



Acetamide behaves in a similar manner and unites with hydrogen chloride, forming the compound acetamide hydrochloride,  $\text{CH}_3\text{CONH}_2.\text{HCl}$ , which is a rather unstable substance:

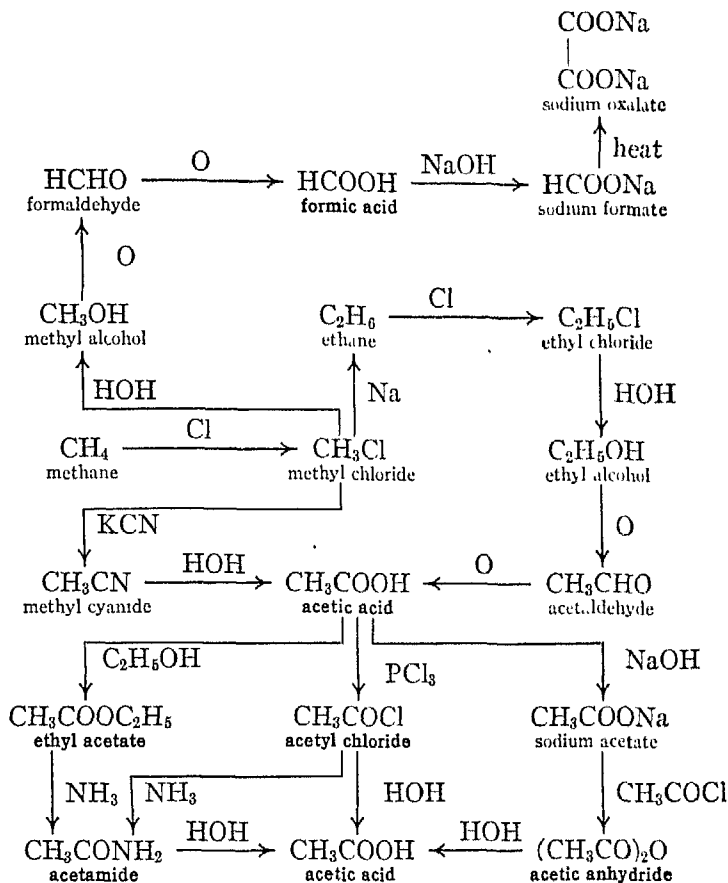


This reaction is characteristic also of compounds containing the amino group.

The acid amides of propionic, butyric, and isobutyric acids are prepared by reactions similar to those used in making acetamide and give reactions characteristic of amides.



## ACIDS, ESTERS, ACID CHLORIDES, ANHYDRIDES, AND AMIDES

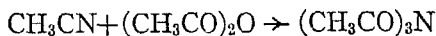


Secondary amides are formed by the interaction of primary amides and anhydrides :



The compound  $(\text{CH}_3\text{CO})_2\text{NH}$  may be regarded as ammonia in which two hydrogen atoms have been replaced by two acetyl groups. The group  $\text{NH}$  is called the *imino group*.

**Tertiary amides** are prepared by treating the alkyl cyanides (nitriles) with anhydrides :



The compound  $(\text{CH}_3\text{CO})_3\text{N}$  may be considered as ammonia in which the three hydrogen atoms have been substituted by three acetyl groups. The three classes of amides may, therefore, be regarded as substituted ammonias.

The esters, acid chlorides, anhydrides, and amides we have studied are derivatives of the monobasic acids. The chart on page 149 shows the synthetic relations between a few of the members of these various series of compounds.

#### QUESTIONS

1. Explain from what compounds acetamide may be considered as derived.
2. How is acetamide prepared?
3. When acetamide is boiled with water, what gas is evolved? What substance remains?
4. What is the amino group? The imino group? How could you convert the amino group in a compound into the hydroxyl group?
5. Write the formula of a hydrochloride. How is such a substance obtained?
6. Write the formula of a secondary and a tertiary amide and explain how these compounds may be considered as derived from ammonia.
7. Write equations showing the preparation of propionamide.

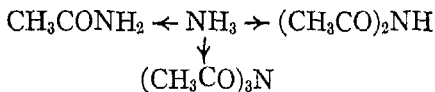
# CHAPTER TEN

## AMINES

SEVERAL groups of compounds which we have studied may be considered as derived from inorganic compounds. The alcohols and ethers, for example, may be regarded as derived from water. By replacing one of the hydrogen atoms in water by the ethyl group we should have ethyl alcohol, and by replacing both hydrogen atoms we should have ether:



The amides may be considered as derived from ammonia. By replacing one or more of the hydrogen atoms in ammonia by the acetyl group we obtain amides:



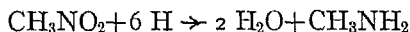
The next group of compounds which we are going to study is called the **amines**. Like the amides there are three classes of amines, which are called primary, secondary, and tertiary.

### AMINES

	NAME	FORMULA	BOILING POINT, °C.
Primary amines	Methyl	$\text{NH}_2\text{CH}_3$	-6
	Ethyl	$\text{NH}_2\text{C}_2\text{H}_5$	19
	Propyl	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	49
Secondary amines	Methyl	$\text{NH}(\text{CH}_3)_2$	7
	Ethyl	$\text{NH}(\text{C}_2\text{H}_5)_2$	56
	Propyl	$\text{NH}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$	98
Tertiary amines	Methyl	$\text{N}(\text{CH}_3)_3$	35
	Ethyl	$\text{N}(\text{C}_2\text{H}_5)_3$	90
	Propyl	$\text{N}(\text{CH}_2\text{CH}_2\text{CH}_3)_3$	156

These three classes of amines may be considered as derived from ammonia by replacing one, two, or three hydrogen atoms in ammonia by alkyl groups. The amines resemble ammonia in their chemical behavior. They are strongly basic substances and give reactions similar to ammonia. The table on the previous page contains a few of these compounds.

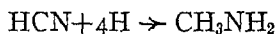
**Methyl amine**,  $\text{CH}_3\text{NH}_2$ , is the simplest primary amine. It contains the amino group ( $\text{NH}_2$ ) and in this respect resembles the primary amides such as acetamide,  $\text{CH}_3\text{CONH}_2$ . Methyl amine may be obtained by reducing nitro methane,  $\text{CH}_3\text{NO}_2$ .



Nitro methane is a nitro compound and contains the nitro group ( $\text{NO}_2$ ). It is made by the interaction of methyl iodide and silver nitrite:



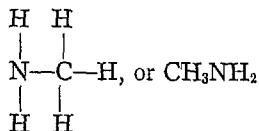
Nitro methane is a colorless liquid which boils at  $101^\circ$ . Methyl amine is also obtained by the reduction of hydrogen cyanide:



Methyl amine is prepared conveniently in the laboratory by the bromination of acetamide in alkaline solution (Hofmann's method). In this reaction brom acetamide,  $\text{CH}_3\text{CONHBr}$ , which is formed as an intermediate product, is decomposed, yielding methyl amine. When methyl amine gas is passed into a solution of hydrogen chloride, the crystalline substance methyl ammonium chloride,  $\text{CH}_3\text{NH}_3\text{Cl}$ , is obtained.

#### EXPERIMENT 33

##### Preparation of methyl amine



and methyl ammonium chloride,  $\text{CH}_3\text{NH}_3\text{Cl}$  (methyl amine hydrochloride)

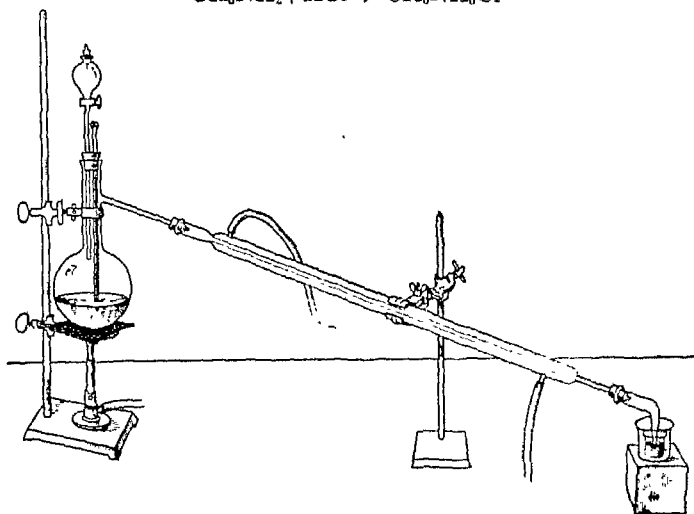
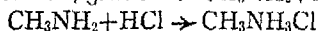
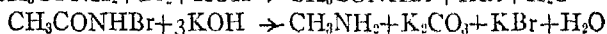
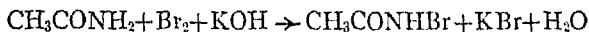


Figure 15

<i>Materials</i>	Solution of 60 grams of potassium hydroxide dissolved in 180 cc. of water
	20 grams acetamide
	18 cc. bromine
	Solution of 25 grams of potassium hydroxide dissolved in 100 cc. of water
	Solution of 40 cc. concentrated hydrochloric acid dissolved in 40 cc. of water
	30 cc. absolute alcohol

*Procedure.* In a 400 cc. beaker dissolve 60 grams of potassium hydroxide in 180 cc. of water, and pour the solution into a 500 cc. distilling flask. The flask is now connected to a condenser. Place a two-hole stopper in the neck of the flask. Through one hole pass a thermometer and adjust it so that the bulb of the thermometer is just below the surface of the alkaline solution in the flask. Through the

other hole place a dropping funnel, which is to hold the yellow-colored solution of monobrom acetamide prepared in the following manner: Place 20 grams of acetamide in a 500 cc. Florence flask and add, under a hood, 18 cc. of bromine. (Be careful that the bromine does not get on your hands.) Now prepare in a beaker an alkaline solution consisting of 25 grams of potassium hydroxide dissolved in 100 cc. of water. This alkaline solution is allowed to cool and is then added gradually to the mixture of acetamide and bromine. During this mixing operation the flask containing the acetamide and bromine should be immersed in cold water and shaken frequently. Should a precipitate separate out, add a small amount of water to dissolve it. When the dark-brown liquid changes to a deep-yellow color, the first reaction has taken place and the mixture consists of a solution of the monobrom derivative of acetamide,  $\text{CH}_3\text{CONHBr}$ , and potassium bromide. The yellow-colored solution is now poured into the dropping funnel of the previously arranged apparatus. An adapter is now joined to the lower end of the condenser and allowed to dip slightly below the surface of about 100 cc. of ice water contained in a beaker. Since the water in the beaker may be drawn back frequently into the condenser, the beaker should rest upon a block of wood which may be removed and the beaker lowered if necessary.

The alkaline solution in the distilling flask is warmed until the thermometer indicates a temperature of  $60^\circ$ . Now allow the solution of monobrom acetamide which is in the dropping funnel to drop gradually into the alkaline solution in the distilling flask. During the mixing of the solutions considerable heat is evolved, and the distilling flask must be cooled from time to time so that the temperature of the alkaline solution in the flask will not exceed  $70^\circ$ . The reaction takes place quietly, and the yellow solution of monobrom acetamide is gradually decolorized. When the solutions have been mixed and the resulting solution is practically colorless, remove the stopper from the distilling flask and introduce a few small pieces of broken glass or pumice stone. These are to prevent bumping during the subsequent distillation. The stopper is now replaced and the flask heated gently over a wire gauze. Pass the methyl amine gas into the ice water to obtain an aqueous solution of it.

Should the water in the beaker be drawn back into the condenser during the distillation, temporarily lower the beaker by removing the wooden block on which it rests, until the end of the adapter is

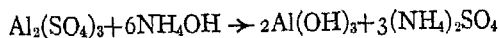
above the surface of the water. When the water which was drawn back has flowed out again into the beaker, raise the beaker to the original position by again placing the block under it. When the distillation of the amine has continued about 2 minutes, replace the beaker of ice water by another beaker containing a solution of 40 cc. concentrated hydrogen chloride dissolved in 40 cc. of water. The beaker containing the solution of hydrogen chloride should be immersed in a larger beaker which contains ice water and is supported by a wooden block. The beaker containing the ice water which has been used to collect the first distillate of methylamine is set aside for Experiments A, B, and C.

The distillation is now continued and the methyl amine gas passed into the cool solution of hydrogen chloride to obtain the solution of methyl ammonium chloride. During this latter part of the distillation the temperature should be raised gradually, and finally the liquid should be boiled until no more of the methyl amine gas passes over, which will require about 40 minutes. The solution of methyl ammonium chloride thus obtained is poured into an evaporating dish and evaporated to dryness on a water bath.

While waiting for the methyl ammonium chloride to evaporate, perform the following tests with the aqueous solution of methyl amine obtained in the first fraction of the distillate:

A. Does the odor resemble that of ammonia? Test the solution with litmus paper. Is it alkaline?

B. Pour 1 cc. of dilute ammonia water (1 : 10) into a test tube, and add a few drops of aluminium sulfate solution (1 : 20). Aluminium hydroxide is precipitated:



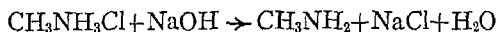
C. Pour 1 cc. of the aqueous amine solution into a test tube and add a few drops of aluminium sulfate solution. Do you get a precipitate similar to the one obtained in the preceding experiment?

When the solution of methyl ammonium chloride has been evaporated to a dry salt, scrape it from the dish with a spatula, powder it, and place it in a dry 100 cc. beaker; add about 30 cc. of hot absolute alcohol, stir, filter, and allow the filtrate to crystallize. Filter off the crystals and dry on layers of filter paper, which should be placed in a desiccator. The crude preparation of methyl ammonium chloride is usually contaminated with a small amount of ammonium chloride.

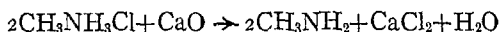
This is due to the fact that ammonia which is formed as a decomposition product in the generating flask distils over with the amine and unites with the hydrogen chloride in the receiver, giving ammonium chloride. Methyl ammonium chloride is separated from the ammonium chloride by treating the mixture with absolute alcohol. This dissolves the methyl ammonium chloride, leaving ammonium chloride, which is insoluble in absolute alcohol.

Calculate the yield of the purified methyl ammonium chloride, preserve a specimen, and perform the following experiments:

*D.* Heat about 0.5 gram of methyl ammonium chloride with 10 cc. of sodium hydroxide solution (1 : 5). Methyl amine is evolved:

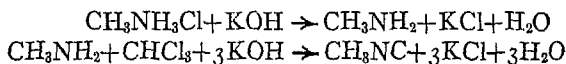


*E.* Place 0.5 gram of dry methyl ammonium chloride in a dry test tube. Add about 2 grams of calcium oxide, and heat. Methyl amine is evolved. Is it inflammable? Test it.



How would ammonium chloride behave when heated with a solution of sodium hydroxide and when heated with calcium oxide?

*F. Isocyanide test for primary amines.* Place about 0.5 gram of methyl ammonium chloride in a test tube. Add 3 drops of chloroform and 2 cc. of an alcoholic solution of potassium hydroxide (1 : 5). Warm the mixture under a hood and note the odor of methyl isocyanide,  $\text{CH}_3\text{NC}$ :



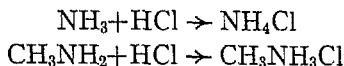
**NOTE.** Usually when liquids are distilled bubbles of vapor are formed easily and regularly in the lower part of the liquid which is in contact with the bottom of the distilling vessel. When distilling certain liquids, or mixtures, bubbles of vapor are not formed easily and regularly in the lower part of the vessel but only at intervals and then with a sudden violence. The result is that the liquid does not distil in the usual manner, but irregularly, and is said to "bump." The bumping can be prevented by placing in the vessel something which will facilitate the formation of bubbles. Pumice stone or small pieces of broken glass or of porous plate are often used for this purpose. The distillation of methyl amine in the experiment above is a good example of a liquid mixture which "bumps" when distilled.

**Reactions of methyl amine.** Methyl amine may be regarded as methane in which one hydrogen atom has been substituted by the amino group,  $\text{CH}_4 \rightarrow \text{CH}_3\text{NH}_2$ . It is usually considered,



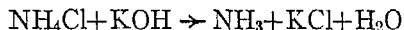
however, as ammonia in which one hydrogen atom has been replaced by the methyl group,  $\text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2$ . Methyl amine is, therefore, a substituted ammonia. Methyl amine behaves like ammonia when treated with various reagents.

Ammonia forms ammonium salts when treated with acids, and methyl amine, which is a substituted ammonia, reacts in a similar manner, forming substituted ammonium salts:

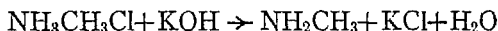


Methyl ammonium chloride,  $\text{CH}_3\text{NH}_3\text{Cl}$ , is a substituted ammonium salt. It is regarded as the methyl derivative of ammonium chloride,  $\text{NH}_4\text{Cl}$ . It is sometimes written  $\text{CH}_3\text{NH}_2\cdot\text{HCl}$  and called *methyl amine hydrochloride*.

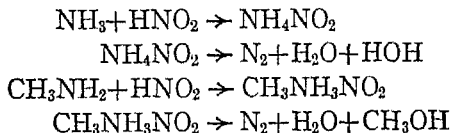
When ammonium salts are boiled with an alkali solution, they are decomposed with evolution of ammonia gas:



Substituted ammonium salts react in a similar manner, giving a substituted ammonia:

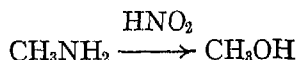


Methyl amine and ammonia behave in a similar manner when treated with nitrous acid. In each case the first product formed is an ammonium salt, and this undergoes decomposition:

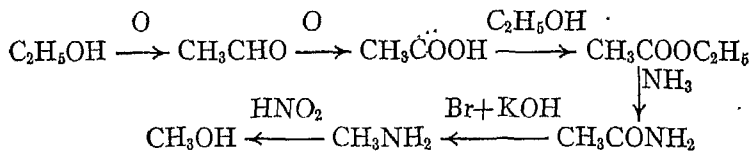


As shown by the reactions above, ammonia reacts with nitrous acid, giving ammonium nitrite, which is decomposed into nitrogen and two molecules of water. Methyl amine, which is a substituted ammonia, reacts in a similar manner with nitrous acid, giving methyl ammonium nitrite,  $\text{CH}_3\text{NH}_3\text{NO}_2$ , which is a substituted ammonium salt. This compound decomposes, giving

nitrogen, one molecule of water, and one molecule of methyl alcohol which may be regarded as a substituted water. In each case the first product formed is decomposed. Thus, by treating an amine with nitrous acid we can replace the amino group by hydroxyl:

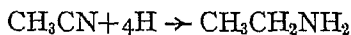


*Synthetic reactions.* By means of Hofmann's method of preparing amines and the reaction of amines with nitrous acid it is possible to pass from a higher member of a series of compounds to a lower member, as shown by the following outline equations:

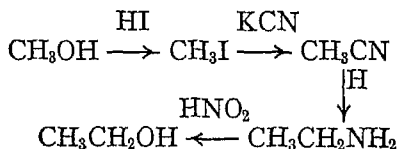


The student should review Experiments 21, 26, 28, 32, and 33. He will observe that with the exception of the reaction of amines with nitrous acid he has performed all the experiments represented by the outline equations above.

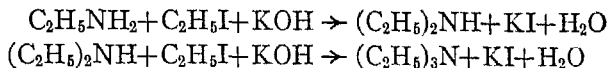
Other primary amines behave in a manner similar to methyl amine and may be prepared by similar reactions. **Ethyl amine**,  $\text{C}_2\text{H}_5\text{NH}_2$ , for example, may be obtained by reducing methyl cyanide:



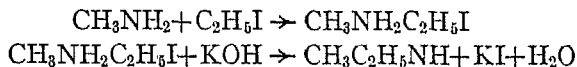
This method of preparing amines by the reduction of alkyl cyanides enables us to build up a higher member of a homologous series from a lower one, as shown by the following outline equations:



**Secondary and tertiary amines.** Secondary amines such as diethyl amine,  $(\text{C}_2\text{H}_5)_2\text{NH}$ , and tertiary amines such as triethyl amine,  $(\text{C}_2\text{H}_5)_3\text{N}$ , may be prepared from primary amines by heating them with an alkyl bromide or iodide in the presence of an excess of potassium hydroxide, as shown by the following reactions:



**Mixed amines** may be obtained by treating in the presence of potassium hydroxide an amine containing a certain alkyl radical with an alkyl halide containing a different alkyl radical:



Thus the compound methyl ethyl amine,  $\text{CH}_3\text{C}_2\text{H}_5\text{NH}$ , is a mixed amine, as it contains two different alkyl radicals.

Methods of preparation and characteristic reactions of amines show that they are substituted ammonias. Amines such as methyl and ethyl amines differ from ammonia in that they are inflammable. Amines which have low molecular weights, such as the primary and secondary methyl amines, are gases. Amines of higher molecular weights are liquids or solids.

### QUESTIONS

1. What kind of compounds are amines?
2. Complete the equations:
  - a. methyl cyanide + hydrogen  $\rightarrow$ .
  - b. nitro methane + hydrogen  $\rightarrow$ .
3. Explain Hofmann's method of preparing amines.
4. How is methyl ammonium chloride prepared and purified?
5. Explain, with equations, the similarity in behavior of ammonia and methyl amine; of ammonium chloride and methyl ammonium chloride.
6. Complete the following outline equations:
  - a.  $\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CONH}_2 \rightarrow \text{CH}_3\text{Cl}$ .
  - b.  $\text{CH}_3\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{I}$ .
7. Write the complete structural formulas of propyl amine and ethyl methyl amine.
8. Explain the laboratory preparation of ethyl amine hydrochloride from propanamide.

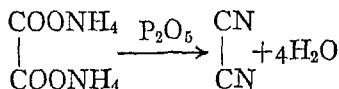
## CHAPTER ELEVEN

### CYANOGEN COMPOUNDS

CYANOGEN compounds are those which contain the univalent cyanogen radical (CN). The simplest of these compounds is

cyanogen,  $\begin{array}{c} \text{C}\equiv\text{N} \\ | \\ \text{C}\equiv\text{N} \end{array}$ , or (CN)<sub>2</sub>, which consists of two cyanogen radicals united together.

Cyanogen may be obtained by heating ammonium oxalate,  $\begin{array}{c} \text{COONH}_4 \\ | \\ \text{COONH}_4 \end{array}$ , with phosphorus pentoxide:



Cyanogen is prepared easily in the laboratory by heating mercuric cyanide.

#### EXPERIMENT 34

##### Preparation of cyanogen, (CN)<sub>2</sub>

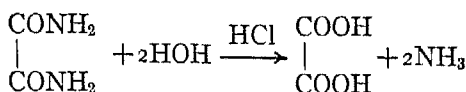
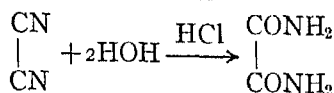


*Procedure.* Heat about 1 gram of mercuric cyanide in a test tube and light the gas which is evolved.

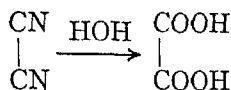
Cyanogen is a colorless, poisonous gas which has a peculiar, pungent odor. It burns with a characteristic peach-colored flame, giving mostly carbon dioxide and nitrogen as oxidation products. The molecular weight of cyanogen, obtained from the vapor density determination, shows that the molecular formula must be as represented above. Explain how the molecular weight determines which empirical formula is the true molecular formula.

When cyanogen is treated with an aqueous solution of hydrogen chloride, it is hydrolyzed to oxamide,  $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{array}$ , which is fur-

ther hydrolyzed to oxalic acid,  $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$  :

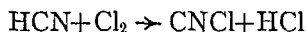


A nitrile is a compound which when hydrolyzed yields an acid. Since cyanogen may be converted into oxalic acid by hydrolysis, it is therefore the nitrile of oxalic acid. As shown by the reactions above, the cyanogen group when hydrolyzed is converted into the carboxyl group :

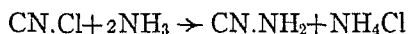


This is a general reaction for compounds containing the cyanogen group.

**Cyanogen chloride**,  $\text{CN}.\text{Cl}$ , is a poisonous liquid formed by the action of chlorine on an aqueous solution of hydrogen cyanide :

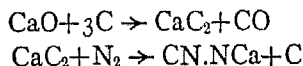


**Cyanamide**,  $\text{CN}.\text{NH}_2$ , is obtained by the interaction of ammonia and cyanogen chloride :

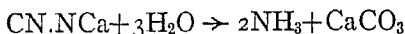


It is a crystalline substance and forms derivatives such as silver cyanamide,  $\text{CN}.\text{NAg}_2$ .

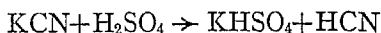
**Calcium cyanamide**,  $\text{CN}.\text{NCa}$ , is obtained by heating carbon and lime in an atmosphere of nitrogen. The calcium carbide,  $\text{CaC}_2$ , which is formed as an intermediate product, reacts with nitrogen, yielding calcium cyanamide :



Calcium cyanamide is manufactured commercially for use as a fertilizer. When placed on the soil it is decomposed slowly by water and ammonia is evolved:

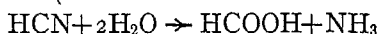


**Hydrogen cyanide** (hydrocyanic acid or prussic acid),  $\text{HCN}$ , occurs in certain plants and is formed by the decomposition of amygdalin, which is a glucoside that occurs in the leaves of the cherry and laurel, in bitter almonds, and in the kernels of peach stones and cherries. It may be prepared by distilling potassium cyanide or potassium ferrocyanide with dilute sulfuric acid:

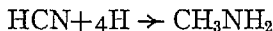


Pure hydrogen cyanide is a colorless liquid boiling at  $25^\circ$ . It has the odor of bitter almonds, burns with a pale-blue flame, and is exceedingly poisonous. Hydrogen peroxide may be used as an antidote to counteract the poisonous effects of this substance.

When hydrogen cyanide is hydrolyzed in alkaline solution, it is converted into formic acid:

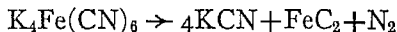


Here, as in the hydrolysis of cyanogen, the cyanogen group is changed into the carboxyl radical. When reduced with nascent hydrogen, hydrogen cyanide yields methyl amine:

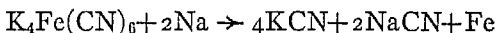


Although the structure of hydrogen cyanide is uncertain, it is customary to represent the formula as  $\text{H}-\text{C}\equiv\text{N}$ .

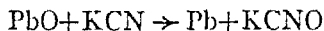
**Potassium cyanide**,  $\text{KCN}$ , is obtained by heating potassium ferrocyanide:



It is also prepared by fusing potassium ferrocyanide with sodium:

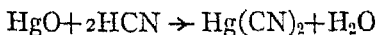


Potassium cyanide is a crystalline substance which is soluble in water and is very poisonous. It is used to extract gold from its ores by the cyanide process. It is also used to reduce metallic oxides such as lead oxide :



When potassium cyanide is treated with silver nitrate, it forms the double salt  $\text{KAg}(\text{CN})_2$ .

**Mercuric cyanide**,  $\text{Hg}(\text{CN})_2$ , may be obtained by treating mercuric oxide with hydrogen cyanide :



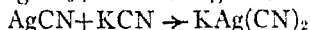
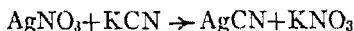
#### EXPERIMENT 35

##### Reactions of cyanides

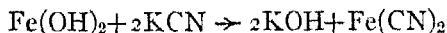
A. In a test tube dissolve 0.5 gram of mercuric cyanide in 5 cc. of water and add about 1 cc. of a solution of silver nitrate (1 : 10). White silver cyanide is precipitated :



B. Dissolve about 0.5 gram of potassium cyanide in 5 cc. of water and add slowly a silver nitrate solution (1 : 10). Silver cyanide is precipitated but dissolves in excess of the potassium cyanide :



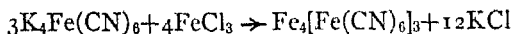
**Potassium ferrocyanide**,  $\text{K}_4\text{Fe}(\text{CN})_6$ , may be prepared from ferrous hydroxide or ferrous sulfate :



It is used in dyeing and in preparing potassium cyanide and potassium ferricyanide.

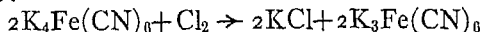
#### EXPERIMENT 36

##### Test for ferrocyanides



*Procedure.* Dissolve a few crystals of potassium ferrocyanide in 2 cc. of water. Add a few drops of a solution of ferric chloride (1 : 10). Prussian blue (ferric ferrocyanide),  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , is precipitated.

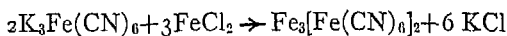
**Potassium ferricyanide**,  $K_3Fe(CN)_6$ , may be made by the interaction of chlorine and an aqueous solution of potassium ferrocyanide:



It is used as a mild oxidizing agent. When treated with ferrous salts, it gives a blue precipitate.

#### EXPERIMENT 37

##### Test for ferricyanides



Pour about 2 cc. of a solution of potassium ferricyanide into a test tube and add a few drops of a solution of ferrous chloride (1:10). Turnbull's blue (ferrous ferricyanide),  $Fe_3[Fe(CN)_6]_2$ , is precipitated.

For a full discussion of cyanogen compounds such as the cyanides, ferrocyanides, and ferricyanides the student should consult the usual standard textbooks of inorganic chemistry.

#### NITRILES AND ISONITRILES

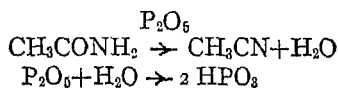
**Nitriles**, or alkyl cyanides, are esters of hydrogen cyanide. **Methyl cyanide**,  $CH_3CN$ , for example, may be considered as the methyl ester of hydrogen cyanide. Alkyl cyanides therefore consist of a radical united to the cyanogen group. These compounds may be obtained by the interaction of alkyl halogen compounds and potassium cyanide:



They are prepared conveniently by distilling the amides, or the ammonium salts of the fatty acids, with a dehydrating agent such as phosphorus pentoxide.

#### EXPERIMENT 38

##### Preparation of methyl cyanide, $CH_3CN$ (Nitrile of acetic acid or acetonitrile)





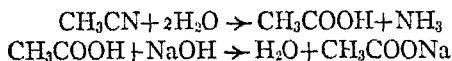
*Materials*  $\left\{ \begin{array}{l} 20 \text{ grams acetamide} \\ 30 \text{ grams phosphorus pentoxide} \end{array} \right.$

*Procedure.* As phosphorus pentoxide absorbs moisture rapidly, it must be weighed very quickly. Weigh rapidly about 15 grams of phosphorus pentoxide on a piece of writing paper. Bend the paper in the shape of a cone. Place the small end of the paper cone in the neck of a 200 cc. distilling flask, and with the aid of a glass rod quickly transfer the pentoxide to the flask. 20 grams of acetamide are now placed in the flask, and then a second portion of about 15 grams of pentoxide is introduced into the flask in the same manner as the first portion. The contents of the flask are now mixed by means of a glass rod, and the flask is connected to a condenser. Place a cork stopper in the neck of the flask and heat carefully with a medium-sized flame, which should be somewhat luminous and kept in constant motion by holding the burner in the hand and rotating it.

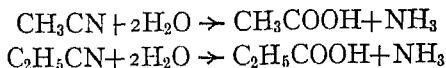
The reaction proceeds with considerable foaming. When the mixture has been heated a few minutes, continue to rotate the flame and gradually increase the size of it so that the nitrile distils slowly. The distillation is discontinued when no more of the nitrile distils over. Add to the distillate about half its volume of water and then solid potassium carbonate until no more dissolves. Pour the liquid into a separating funnel, leaving behind the undissolved carbonate; separate the upper layer of methyl cyanide. This is now poured into a dry 100 cc. distilling flask. Add about 4 grams of phosphorus pentoxide, to complete the dehydration of the nitrile. Place a thermometer in the neck of the flask and distil. Weigh the product obtained. Calculate the yield and preserve a specimen in a sealed tube.

Methyl cyanide boils at  $82^{\circ}$ . It is a colorless liquid which is soluble in water and has a peculiar odor.

*A. Hydrolysis of methyl cyanide.* Heat 1 cc. of methyl cyanide in a test tube with about 8 cc. of sodium hydroxide solution (1:4). Note the odor of the gas evolved.



**Reactions of nitriles and isonitriles.** Alkyl cyanides such as methyl cyanide are hydrolyzed easily in the presence of dilute acids, or alkalis, into acids:

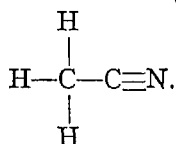


In view of this fact these compounds are often called *nitriles* and named in accordance with the acid they yield when hydrolyzed. Thus, since methyl cyanide yields acetic acid when hydrolyzed, it is therefore the nitrile of acetic acid and is called *acetonitrile*. Ethyl cyanide is likewise called *propionitrile*. Methyl and ethyl cyanides, the lower members of this series of alkyl cyanides, are colorless liquids soluble in water.

When reduced with hydrogen the alkyl cyanides are converted into primary amines :



This fact shows that in the alkyl cyanides the alkyl group is united directly to the carbon atom of the cyanogen group



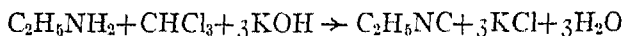
**Isocyanides** are compounds isomeric with the corresponding alkyl cyanides. These compounds are also known as *isonitriles*, or *carbylamines*. In the following table are given the formulas and boiling points of a few of the nitriles, or alkyl cyanides, and the isonitriles, or isocyanides :

NITRILES			ISONITRILES		
Name	Formula	Boiling Point, °C.	Name	Formula	Boiling Point, °C.
Methyl cyanide	$\text{CH}_3\text{CN}$	82	Methyl isocyanide	$\text{CH}_3\text{NC}$	58
Ethyl cyanide	$\text{C}_2\text{H}_5\text{CN}$	97	Ethyl isocyanide	$\text{C}_2\text{H}_5\text{NC}$	78

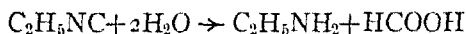
The isonitriles are volatile liquids which have a very disagreeable odor. They may be obtained by the interaction of silver cyanide and alkyl halogen compounds:



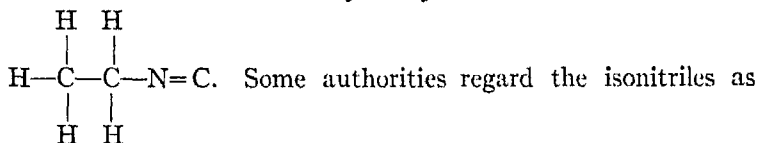
They may also be prepared by heating a primary amine with an alcoholic solution of potassium hydroxide and chloroform (see Experiment 33 F):



The isonitriles are hydrolyzed by solutions of dilute acids yielding an amine and an acid:



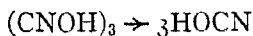
This reaction shows that in the isonitriles the cyanogen group is united to the alkyl radical by means of nitrogen and not by a carbon atom as in the nitriles. When the isonitriles are hydrolyzed, the nitrogen remains in combination with the alkyl radical while the carbon of the cyanogen group leaves the isonitriles. As shown by the reaction above, the chemical behavior of the isonitriles is quite different from that of the nitriles, which yield acids when hydrolyzed. In consequence of this fact it is customary to represent the isonitriles by formulas in which the nitrogen of the cyanogen group is united directly to the alkyl radical. The formula of ethyl isocyanide is therefore



esters of an unknown hydrogen isocyanide,  $\text{HNC}$ , which would be an isomer of hydrogen cyanide.

#### CYANATES AND ISOCYANATES

**Cyanic acid**,  $\text{HOCN}$ , may be prepared by heating cyanuric acid,  $(\text{CNOH})_3$ :



It is an unstable liquid which decomposes above  $0^\circ$ .

Potassium cyanate, KOCN, is formed by the slow oxidation of potassium cyanide in the air. It may be prepared by heating potassium cyanide with an oxide such as litharge and extracting the reaction product with dilute alcohol:



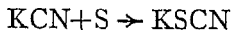
It is a white crystalline substance soluble in water and in dilute alcohol. When a solution of potassium cyanate is added to a solution of ammonium sulfate and the mixture evaporated, the ammonium cyanate,  $\text{NH}_4\text{OCN}$ , which is first formed is gradually converted to urea,  $\text{CO}(\text{NH}_2)_2$ . (See Urea, page 178.) Esters of cyanic acid such as alkyl cyanates have not been isolated, because the reactions which should give them yield other products. However, alkyl isocyanates, such as ethyl isocyanate,  $\text{C}_2\text{H}_5\text{NCO}$ , may be prepared by the interaction of silver cyanate and alkyl halogen compounds:



The alkyl isocyanates are volatile liquids which have a very disagreeable odor.

### THIOCYANATES AND ISOTHIOCYANATES

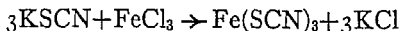
**Thiocyanates**, or **sulfocyanates**, are obtained by heating cyanides with sulfur. Thus *potassium thiocyanate*, KSCN, may be obtained by the interaction of potassium cyanide and sulfur:



Thiocyanic, or sulfocyanic, acid may be obtained by distilling potassium thiocyanate with sulfuric acid. It is an unstable liquid having a penetrating odor. The thiocyanates are used as mordants in dyeing and as test reagents for ferric salts in inorganic analysis.

#### EXPERIMENT 39

##### Test for thiocyanates



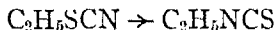
Dissolve in a test tube about 0.5 gram of potassium thiocyanate in 2 cc. of water. To this solution add a few drops of a ferric chloride

solution (1:10). A blood-red color due to the presence of ferric thiocyanate is produced.

Esters of thiocyanic acid, such as methyl thiocyanate,  $\text{CH}_3\text{SCN}$ , are obtained by the interaction of thiocyanates and alkyl iodides:



By heating alkyl thiocyanates an intramolecular change occurs and alkyl isothiocyanates are obtained. Thus, by distilling ethyl thiocyanate,  $\text{C}_2\text{H}_5\text{SCN}$ , *ethyl isothiocyanate*,  $\text{C}_2\text{H}_5\text{NCS}$ , is obtained:



The isothiocyanates form a series of compounds similar to the alkyl isocyanates and are derived from hypothetical isothiocyanic acid,  $\text{HNCS}$ , which has not been isolated. These compounds are commonly called "mustard oils," because mustard seeds contain a glucoside from which allyl isothiocyanate,  $\text{CH}_2:\text{CHCH}_2\text{N}:\text{CS}$ , was first obtained.

### QUESTIONS

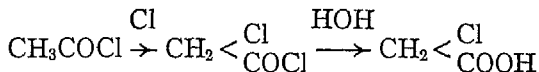
1. What kind of substances are cyanogen compounds?
2. How is cyanogen prepared?
3. Why is the formula of cyanogen written  $\text{C}_2\text{N}_2$ ?
4. What are nitriles?
5. When a nitrile is hydrolyzed, what becomes of the cyanogen radical?
6. What is calcium cyanamide, and for what purpose is it used?
7. How are ferrocyanides and ferricyanides tested?
8. Explain the laboratory preparation of methyl cyanide.
9. Write equations showing how nitriles and isonitriles may be prepared.
10. Write equations showing the behavior of nitriles and isonitriles when hydrolyzed.
11. Write the formula of ethyl isocyanate, methyl thiocyanate, and ethyl isothiocyanate.
12. How are thiocyanates tested?
13. Write the formulas of the nitriles of oxalic and acetic acids.
14. Explain the preparation of the nitrile of propionic acid.
15. Write the following outline reactions showing intermediate products:
  - a.  $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{NH}_2$ .
  - b.  $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$ .

## CHAPTER TWELVE

### SUBSTITUTED ACIDS

#### HALOGEN AND AMINO SUBSTITUTED ACIDS AND DERIVATIVES

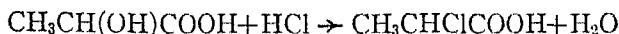
IN the study of the structure of acetic acid, attention was called to the fact that it consists of an alkyl radical (methyl) united to a carboxyl group. When substitution takes place in the carboxyl group of the compound, we have an acid derivative. Thus sodium acetate,  $\text{CH}_3\text{COONa}$ , is a derivative of acetic acid formed by replacing the hydrogen of the carboxyl group by sodium. When substitution takes place in the methyl radical of acetic acid, we have compounds formed which are known as *substituted acids*. When acetic acid interacts with chlorine, we obtain as the first product of the action monochlor acetic acid,  $\text{CH}_2 < \overset{\text{Cl}}{\text{COOH}}$  which is regarded as a substituted acetic acid. Monobrom acetic acid,  $\text{CH}_2 < \overset{\text{Br}}{\text{COOH}}$ , obtained by the interaction of acetic acid and bromine, is also a substituted acid. As it is easier to introduce a halogen atom into an acid chloride than into the acid itself, and as substituted acid chlorides are easily hydrolyzed into the corresponding substituted acids, the acid chlorides, or bromides, are frequently used in preparing the chlor, or brom, substituted acids:



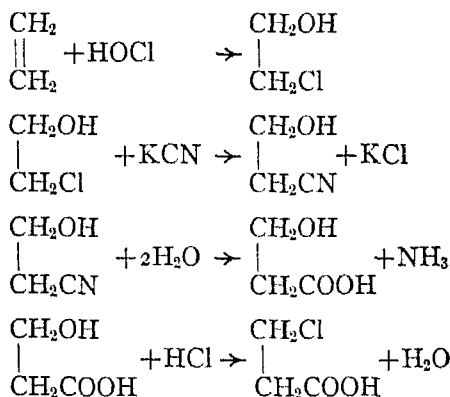
As shown by the outline reactions above, acetyl chloride reacts with chlorine, forming chlor acetyl chloride,  $\text{CH}_2 < \overset{\text{Cl}}{\text{COCl}}$ , which when hydrolyzed yields chlor acetic acid.

By the continued action of chlorine on acetic acid, dichlor acetic acid,  $\text{CHCl}_2\text{COOH}$ , and trichlor acetic acid,  $\text{CCl}_3\text{COOH}$ , are obtained. These substituted acids yield derivatives such as salts and esters, similar to those obtained from the ordinary acids.

As previously explained (see Propionic acid, page 126), the monohalogen substituted propionic acids exist in isomeric forms. Alpha chlor propionic acid may be prepared by the interaction of lactic acid and hydrogen chloride :



Beta chlor propionic acid may be obtained from ethylene by the following series of reactions :



As shown by the equations above, ethylene unites with hypochlorous acid, giving ethylene chlorhydrin,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{Cl} \end{array}$ . This com-

pound then reacts with potassium cyanide, yielding ethylene cyanhydrin,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{CN} \end{array}$ , which when hydrolyzed is converted into

beta hydroxy propionic acid,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ . This substance then reacts with hydrogen chloride, giving beta chlor propionic acid.

**Amino substituted acids.** We can substitute the hydrogen atoms of the alkyl group in acetic and propionic acids not only by halogen atoms, forming halogen substituted acids, but we

can also replace these atoms by other atoms, or groups, such as the amino ( $\text{NH}_2$ ) group, forming amino substituted acids. A number of amino acids are natural decomposition products of the proteins, which are highly complex substances present in plants and animals, and consequently they are compounds of considerable physiological importance.

In the following table are given a few of the simpler chlor and amino substituted acids and the monobasic acids from which they are derived :

MONOBASIC ACIDS	SUBSTITUTED ACIDS	
	Monochlor Acids	Monoamino Acids
$\text{CH}_3\text{COOH}$ acetic acid	$\text{CH}_2\text{ClCOOH}$ chlor acetic acid	$\text{CH}_2\text{NH}_2\text{COOH}$ amino acetic acid (glycocoll)
$\text{CH}_3\text{CH}_2\text{COOH}$ propionic acid	$\text{CH}_3\text{CHClCOOH}$ alpha chlor propionic acid	$\text{CH}_3\text{CHNH}_2\text{COOH}$ alpha amino propionic acid (alpha alanine)
	$\text{CH}_2\text{ClCH}_2\text{COOH}$ beta chlor propionic acid	$\text{CH}_2\text{NH}_2\text{CH}_2\text{COOH}$ beta amino propionic acid (beta alanine)

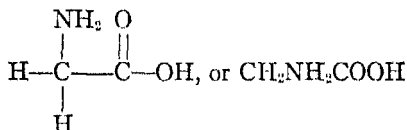
In general these amino acids may be obtained by treating the monohalogen substituted acids with ammonia.

**Amino acetic acid**, (glycocoll or glycine)  $\text{CH}_2 < \begin{smallmatrix} \text{NH}_2 \\ \text{COOH} \end{smallmatrix}$ , is the first member of this group of amino acids. It is prepared by the interaction of chlor acetic acid and ammonia. The ammonium salt of amino acetic acid which is thus obtained is treated with moist copper oxide, yielding copper glycocoll,  $(\text{CH}_2\text{NH}_2\text{COO})_2\text{Cu}$ . The interaction of copper glycocoll and hydrogen sulfide yields glycocoll.

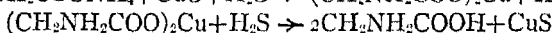
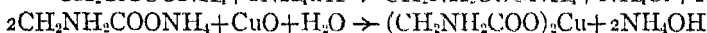
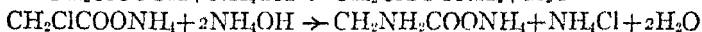
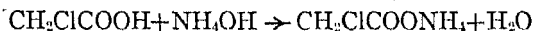


## EXPERIMENT 40

Preparation of amino acetic acid  
(Glycocoll or Glycine)



and copper amino acetate, (copper glycocoll)  $(\text{CH}_2\text{NH}_2\text{COO})_2\text{Cu}$



<i>Materials</i>	{ 10 grams monochlor acetic acid
	{ 10 cc. water
	{ 120 cc. concentrated ammonia
	{ Solution of 40 cc. of concentrated hydrochloric acid dissolved in 150 cc. of water
	{ 14 grams of copper sulfate
	{ 4 grams of aluminium sulfate

*Procedure.* Pour 120 cc. of concentrated ammonium hydroxide into a liter flask. Add a solution of 10 grams of monochlor acetic acid dissolved in 10 cc. of water. (*Caution!* Do not get the monochlor acetic acid on your hands.) Shake the mixture thoroughly, place a cork stopper in the neck of the flask, and allow to stand about 24 hours.

Steam is now passed into the mixture to eliminate the excess of ammonia which is absorbed in a solution of hydrogen chloride. This operation is carried out in the following manner: Arrange an apparatus as shown in Figure 16. Flask *A*, containing about 500 cc. of water, is fitted with a safety tube, *C*, and the exit tube is connected to flask *B*. The latter flask, which is connected to a condenser, is placed in an inclined position so that when the liquid rolls about in the flask during the distillation it does not touch the exit tube of flask *B*, and consequently is not carried over mechanically with the steam. The mixture of ammonia and monochlor acetic acid is placed in flask *B*, and the entire apparatus adjusted. Both flasks are heated over wire gauzes with Bunsen burners. Steam from the boiling water

in the first flask is passed into the liquid in the second flask in order to drive out the excess of ammonia which is contained in the mixture

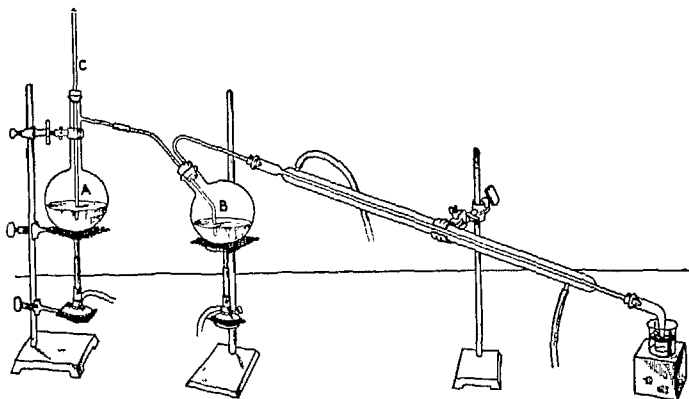
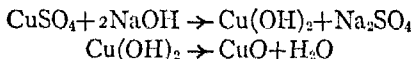


Figure 16

of ammonia and monochloroacetic acid. An adapter is fitted to the end of the condenser, and the end of the adapter is allowed to dip below the surface of a solution consisting of 40 cc. of commercial concentrated hydrogen chloride dissolved in 150 cc. of water. The beaker containing the solution of hydrochloric acid should be immersed in a large beaker containing ice water. The object of this acid solution is to absorb and neutralize the ammonia which is given off during the heating and thus prevent it from escaping into the air and making the atmosphere of the laboratory unpleasant. Should the acid solution in the beaker be drawn back into the condenser, it may be made to flow out again by temporarily lowering the beaker until the surface of the acid solution is below the end of the adapter. The distillation is continued until the excess of ammonia is completely eliminated from the mixture, which will require about 1.5 hours.

The apparatus is now disconnected. If the excess of ammonia has been driven out entirely during the distillation, the reaction product remaining in flask B should no longer have an ammoniacal odor. Pour the reaction product, consisting of a solution of aminoacetic acid and ammonium chloride, into an evaporating dish, and warm over a wire gauze. Add to it moist copper oxide prepared in the following manner:

Fourteen grams of powdered copper sulfate are dissolved in about 200 cc. of hot water. Heat the solution until it boils, and then add a rather concentrated solution of sodium hydroxide until the black hydrated copper oxide is completely precipitated. Filter, and wash several times with hot water:



When the solution of amino acetic acid has been treated with the copper oxide, the mixture is boiled about 10 minutes, with constant stirring, after which it is filtered. The filtrate is evaporated somewhat if necessary and allowed to crystallize. The crystals of copper glycoll are filtered off and a portion dried on layers of filter paper and preserved as a specimen.

Glycoll may be prepared from the copper salt, in the following manner:

Treat the copper glycoll with an amount of hot water just sufficient to dissolve it, and add to the solution about 5 grams of aluminium hydroxide prepared as directed below; heat the solution until it boils, and pass in hydrogen sulfide until the solution is saturated. Filter, and wash with water saturated with hydrogen sulfide. Evaporate the filtrate to a small volume, and allow the glycoll to crystallize. Preserve a specimen.

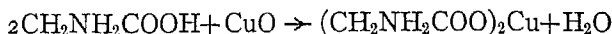
Glycoll is a sweet substance which crystallizes in colorless prisms and melts at  $23.2^\circ$  with decomposition.

*NOTE.* Hydrogen sulfide may be obtained from the laboratory supply apparatus or may be prepared by placing about 40 grams of ferrous sulfide in a filtering flask and allowing sulfuric acid (1:3) to drop upon it from a dropping funnel. The hydrogen sulfide which emerges from the side tube of the filtering flask is conducted into a wash bottle containing water and then into the solution of copper glycoll.

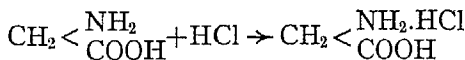
The aluminium hydroxide is added to prevent the formation of a colloidal solution of copper sulfide, which is difficult to filter. It is prepared by dissolving about 4 grams of powdered aluminium sulfate in about 40 cc. of hot water and adding concentrated ammonia until the aluminium hydroxide is completely precipitated. The precipitate is filtered and washed with water.

A. Dissolve 0.5 gram of glycoll in about 5 cc. of water, and add 1 cc. of a solution of ferric chloride (1:10). The solution is colored deep-red.

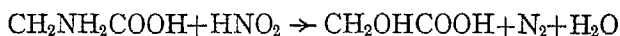
The amino acids are crystalline substances containing the carboxyl and amino groups and show the characteristic reactions of these groups by forming salts with both acids and bases. They are neutral substances, because the basic amino group neutralizes the acidity of the carboxyl group. Glycocoll, for example, gives a neutral reaction with litmus and reacts with the oxides or hydroxides of the heavy metals, forming salts in which the hydrogen of the carboxyl group is replaced by the metal:



When glycocoll is treated with acids, it behaves like an amine and forms substituted ammonium salts. Thus glycocoll hydrochloride,  $\text{CH}_2 < \begin{smallmatrix} \text{NH}_2 \cdot \text{HCl} \\ \text{COOH} \end{smallmatrix}$ , is formed by the interaction of glycocoll and hydrochloric acid:

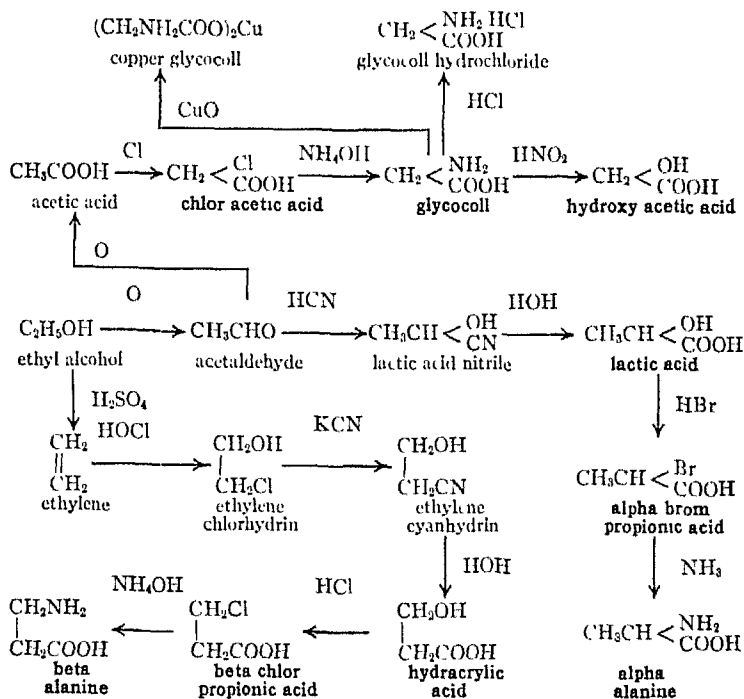


When treated with nitrous acid the amino group in glycocoll is replaced by hydroxyl, as in the case of amines, forming the compound hydroxy acetic acid,  $\text{CH}_2 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ :



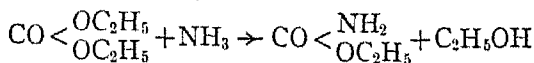
**Amino propionic acids.** The isomeric monoamino derivatives of propionic acid may be prepared from the corresponding halogen acids by treating them with ammonia. Alpha amino propionic acid is called *alpha alanine*, and beta amino propionic acid is known as *beta alanine*. These compounds show the usual chemical behavior of amino acids; that is, they form salts with both acids and bases and react with nitrous acid, yielding hydroxy acids. In addition to the chlor and amino substituted acids which have been mentioned, there are a number of other different classes of substituted acids. Some of these will be considered later. The following outline equations show how the substituted acids we have considered may be obtained from ethyl alcohol:

## SUBSTITUTED ACIDS



## UREA, URIC ACID, AND RELATED COMPOUNDS

The simplest amino would be amino formic acid,  $\text{NH}_2\text{COOH}$ , which is also called carbamic acid. This compound has not been isolated, although certain derivatives of it have been prepared. Ammonium carbamate,  $\text{NH}_2\text{COONH}_4$ , is obtained by treating carbon dioxide with ammonia. The esters of carbamic acid are known as *urethanes*, because they are closely related to urea. *Urethane*, or ethyl carbamate,  $\text{NH}_2\text{COOC}_2\text{H}_5$ , may be prepared by the interaction of ethyl carbonate and ammonia:

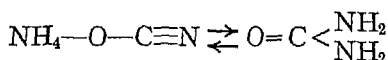


It is a crystalline compound, melting at  $50^\circ$ .

**Urea** (carbamide),  $\text{NH}_2\text{CONH}_2$ , or  $\text{CO} < \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$ , is the acid amide of carbamic acid. Urea occurs in the urine of mammals and is a compound of considerable physiological importance. The waste nitrogenous products of mammals are excreted in the urine mainly in the form of urea. Human urine contains about 3 per cent of urea, and an adult excretes about 25 grams of urea per day. Urea may be obtained from urine by evaporating the urine to a small volume and adding concentrated nitric acid, which precipitates urea nitrate,  $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$ . The urea nitrate is purified by dissolving in water and reprecipitating with nitric acid, after which it is filtered and decomposed with barium carbonate:



Urea was first prepared in the laboratory by Wöhler (1828), who obtained it by evaporating an aqueous solution of ammonium cyanate,  $\text{NH}_4\text{OCN}$ . When an aqueous solution of ammonium sulfate and potassium cyanate is evaporated, ammonium cyanate is formed as the first product of the reaction, and this then undergoes an intramolecular rearrangement, forming urea:

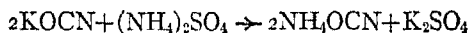


The reaction is reversible, and therefore the forward action is not entirely completed. Ammonium cyanate and urea are isomeric compounds, and in the conversion of ammonium cyanate into urea the molecule of ammonium cyanate undergoes an intramolecular rearrangement — that is, a rearrangement of the atoms within the molecule. Wöhler's discovery that urea, an organic compound, could be prepared from ammonium cyanate, an inorganic compound, was of great historical importance; as it was the first example of the laboratory preparation of an organic compound from inorganic materials. Previous to this discovery it was thought that organic compounds were always

produced in living bodies under the influence of the so-called "vital force." This discovery showed, then, that the influence of a living organism is not necessary for the production of organic compounds. It was many years, however, before laboratory methods of synthetic organic chemistry were well established.

## EXPERIMENT 41

Preparation of urea,  $\text{O}=\text{C} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$

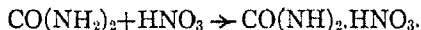


Materials  $\left\{ \begin{array}{l} 12 \text{ grams potassium cyanate} \\ 24 \text{ grams ammonium sulfate} \\ 18 \text{ cc. absolute alcohol} \end{array} \right.$

*Procedure.* Treat 12 grams of powdered potassium cyanate with a sufficient amount of water to dissolve it, and pour the solution into a porcelain evaporating dish. Add a solution prepared by dissolving 24 grams of powdered ammonium sulfate in 30 cc. of water. Place the dish upon a water bath, and evaporate the mixture to dryness. With the aid of a spatula scrape the residue into a mortar, powder it, and place it in a 100 cc. flask. Add about 18 cc. of absolute alcohol. In the neck of the flask place a cork stopper through which passes a glass tube serving as an air condenser. Place the flask on a hot-water bath and allow it to remain there until the alcohol has boiled a few minutes. Pour the hot alcohol through a filter, leaving the residue in the flask. Repeat the alcohol extraction several times to dissolve out most of the urea, leaving the insoluble potassium sulfate. The filtrates are combined, placed in an evaporating dish, and evaporated to dryness.

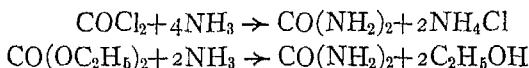
Urea crystallizes in colorless needles, melts at  $132^\circ$ , and is soluble in water and alcohol. Calculate the yield and preserve a specimen.

A. To 1 cc. of a concentrated solution of urea in a test tube add a few drops of concentrated nitric acid. The crystalline urea nitrate is deposited:



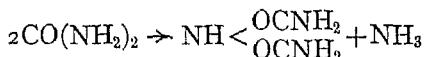
How would a compound like methyl amine, which also contains an amino group, react with nitric acid?

Urea may also be prepared by treating carbonyl chloride,  $\text{COCl}_2$ , or ethyl carbonate,  $\text{CO}(\text{OC}_2\text{H}_5)_2$ , with ammonia :

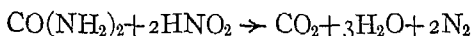


These reactions are analogous to those used in preparing acetamide from acetyl chloride or ethyl acetate. Urea may, therefore, be regarded as the diamide of carbonic acid,  $\text{O}=\text{C} < \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$ .

**Reactions of urea.** Urea gives certain characteristic reactions. When it is heated to a temperature of about  $155^\circ$  it is decomposed, and biuret,  $\text{NH}_2\text{CO.NH.CONH}_2$ , a crystalline substance, is obtained as one of the decomposition products :



An aqueous solution of biuret reacts with an alkaline copper sulfate solution, giving a characteristic reddish-violet coloration. This test is known as the *biuret reaction*. Urea, like other amides, forms salts such as urea nitrate when treated with acids (Experiment 41 A, page 179). When treated with nitrous acid urea is decomposed, yielding carbon dioxide, water, and nitrogen :



Similar decomposition products are obtained by the interaction of urea with solutions of hypobromites or hypochlorites :



The amount of urea in a sample of urine may be estimated quantitatively in accordance with the reaction above by measuring the volume of nitrogen evolved. When a solution of urea is allowed to stand for some time, the urea is gradually hydrolyzed and ammonia is evolved :

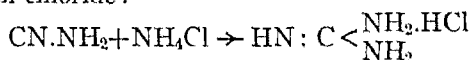


Thus, the odor of ammonia is often observed in urinals or stables which are not thoroughly clean. When an acid, or alkaline,

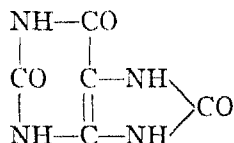


solution of urea is boiled, the urea is hydrolyzed in a similar manner.

**Compounds related to urea.** There are a number of complex nitrogen compounds closely related to urea. *Guanidine*,  $\text{HN} : \text{C}(\text{NH}_2)_2$ , a colorless crystalline substance, may be regarded as urea in which the oxygen atom has been replaced by the imino (NH) group. It may be prepared in the form of its hydrochloride by the interaction of an alcoholic solution of cyanamide and ammonium chloride :



**Uric acid**,  $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ , is a complex derivative of urea containing two urea residues, as shown by the following structural formula :



It contains no carboxyl groups, yet it acts like an acid because two of its hydrogen atoms may be replaced by metals, forming salts such as the disodium salt  $\text{C}_5\text{H}_2\text{Na}_2\text{N}_4\text{O}_3$ . Uric acid is a colorless crystalline substance. It occurs in the human urine in small quantities and is found in the excrement of birds and reptiles in the form of ammonium urates. In certain diseases such as gout and rheumatism the amount of uric acid in the body is increased, and as the acid is very insoluble, it is deposited in the joints of the body and in the pelvis of the kidney and bladder in the form of insoluble stones which consist of uric acid or a very insoluble acid salt of uric acid.

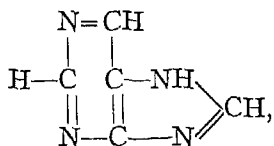
#### EXPERIMENT 42

##### Murexide test for uric acid

Place about 0.5 gram of uric acid in a small evaporating dish, and add 0.5 cc. of concentrated nitric acid. Evaporate the mixture to

dryness on a water bath and add to the dry residue 2 drops of a dilute ammonia solution (1 : 10). The color of the residue becomes purplish-red.

There are a number of important compounds which have structural formulas similar to uric acid. *Purine*, which has the formula



may be regarded as the substance from which uric acid is derived. Purine yields other important derivatives, such as xanthine, which occurs in the tissues of the body, and theobromine, which is obtained from cocoa beans and is a constituent of chocolate. Caffeine and guanine are also derivatives of purine. Caffeine is present in coffee and tea. Guanine is obtained from guano.

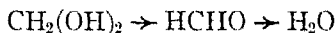
### QUESTIONS

1. Explain, with examples, the difference between an acid derivative and a substituted acid.
2. Explain, with equations, the laboratory preparation of copper glycoll and amino acetic acid.
3. Explain, with equations, the general chemical behavior of amino acids.
4. Write the complete structural formula of alpha amino propionic acid.
5. Write the following outline equations: ethyl alcohol  $\rightarrow$  glycoll.
6. Explain the laboratory preparation of urea. What is the historical importance of this reaction?
7. Name some of the nitrogen compounds which are related to urea.

## CHAPTER THIRTEEN

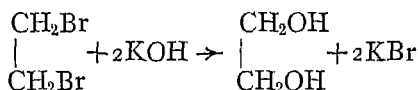
### POLYHYDROXYL DERIVATIVES AND RELATED COMPOUNDS

We have studied compounds such as methyl and ethyl alcohol which contain one hydroxyl group. Now there are a number of substances which contain more than one hydroxyl group. These polyhydroxyl compounds, or complex alcohols, give reactions which are characteristic of the simple alcohols. The dihydroxy derivatives of the paraffin hydrocarbons are known as *glycols*. The simplest member of this group of compounds would be methylene glycol,  $\text{CH}_2(\text{OH})_2$ , which is dihydroxy methane. This substance, however, does not exist, since two hydroxyl groups united to one carbon atom give an unstable structure:

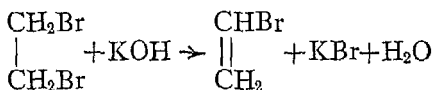


Ethylene glycol,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , is the simplest of the glycols. It is the symmetrical dihydroxy derivative of ethane. Unsymmetrical dihydroxy ethane,  $\begin{array}{c} \text{CH}(\text{OH})_2 \\ | \\ \text{CH}_3 \end{array}$ , does not exist because a compound which has this formula would have two hydroxyl groups united to one carbon atom and this is an unstable condition. The table on the following page contains the complete and abbreviated structural formulas of ethylene glycol, glycerol, and their boiling points. There are also included the hydrocarbons from which these two polyhydroxyl compounds are derived.

Ethylene glycol is a colorless liquid which has a sweet taste, is soluble in water and alcohol, and boils at  $197^\circ$ . It may be prepared by boiling ethylene dibromide, or ethylene dichloride, with dilute aqueous solutions of the hydroxides, or carbonates, of sodium or potassium:



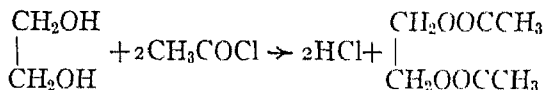
When concentrated solutions of alkalis are used, ethylene dibromide is decomposed, yielding monobrom ethylene:



## HYDROCARBONS AND POLYHYDROXYL COMPOUNDS

HYDROCARBONS	POLYHYDROXYL COMPOUNDS	STRUCTURAL FORMULA		BOILING POINT, °C
		Complete	Abbreviated	
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \\ \text{ethane} \end{array}$	Ethylene glycol	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \\ \text{or} \\ \text{CH}_2\text{OH}.\text{CH}_2\text{OH} \end{array}$	197
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \\ \text{propane} \end{array}$	Glycerol	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OH} \\ \text{or} \\ \text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH} \end{array}$	290

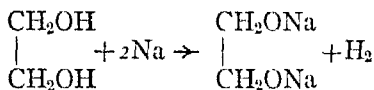
Ethylene glycol contains two hydroxyl radicals and consists of two primary alcohol groups united together. It gives reactions which are characteristic of compounds containing primary alcohol groups, and one or both of the hydroxyl groups may be acted upon in these reactions. When ethylene glycol is treated with acetyl chloride, two molecules of hydrogen chloride are evolved:



This reaction shows the presence of two hydroxyl groups. Since two hydroxyl groups united to one carbon atom give an unstable condition, the two hydroxyl groups must be united to different carbon atoms, and consequently ethylene glycol has

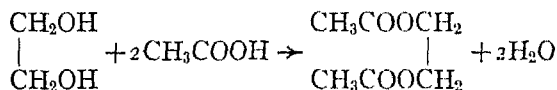
the formula  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ . The interaction of ethylene glycol and

sodium gives the disodium derivative of ethylene glycol:



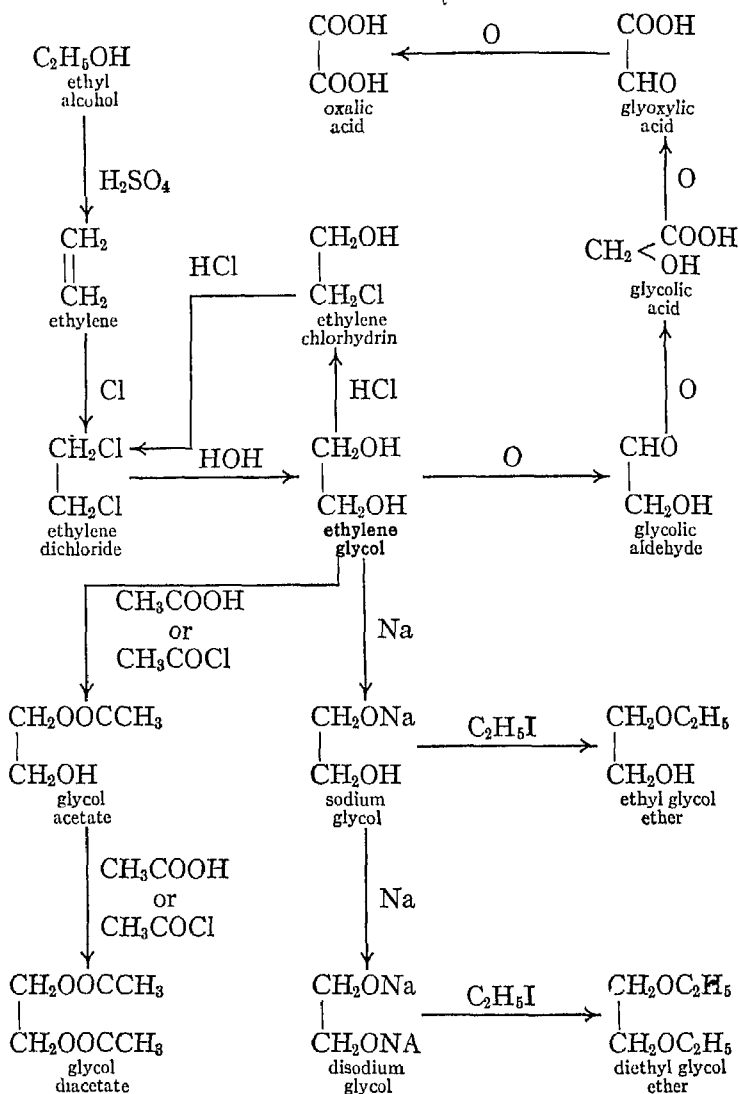
When treated with acetic acid it yields the ethylene glycol ester

of acetic acid (ethylene glycol diacetate)  $\begin{array}{c} \text{CH}_2\text{OOCCH}_3 \\ | \\ \text{CH}_2\text{OOCCH}_3 \end{array}$ :



The outline equations on the following page show the general chemical behavior of ethylene glycol. As shown by these outline equations, ethylene glycol behaves in a manner similar to ethyl alcohol, from which it may be obtained. When treated with hydrogen chloride, either one or both hydroxyl groups are replaced by chlorine. By the interaction of ethylene glycol and acetic acid, or acetyl chloride, either an acetate or a diacetate may be obtained. The hydrogen atoms of the hydroxyl groups may be replaced by sodium, and these sodium compounds yield ethers when treated with alkyl iodides. When oxidized, each primary alcohol group of ethylene glycol is oxidized to an aldehyde group, which on further oxidation is converted to a carboxyl group. The general chemical properties of these various derivatives of ethylene glycol and the exact laboratory

## ETHYLENE GLYCOL AND DERIVATIVES



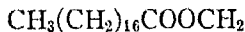
methods of preparing these compounds may be ascertained by consulting the usual reference books.

**Hydroxyl derivatives of propane.** Propane,  $\text{CH}_3\text{CH}_2\text{CH}_3$ , yields two isomeric monohydroxyl derivatives, which are normal propyl alcohol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , and isopropyl alcohol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ . Dihydroxyl derivatives of propane, such as alpha beta propylene glycol,  $\text{CH}_3\text{CHOH}\cdot\text{CH}_2\text{OH}$ , and trimethylene glycol,  $\text{CH}_2\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ , also have been prepared. These compounds have a chemical behavior very similar to ethylene glycol and are not substances of special importance.

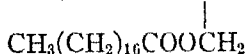
**Glycerol** (glycerine, or symmetrical trihydroxy propane),  $\text{CH}_2\text{OH}$

$\begin{array}{c} | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , or  $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CH}_2\text{OH}$ , occurs naturally in fats

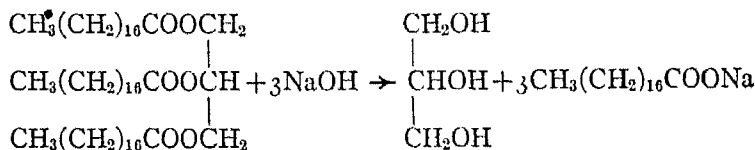
and oils as the glycerol esters of certain monobasic acids. Glycerol is prepared commercially from tallow and other fats. Tallow is the fat extracted from cattle, sheep, or horses and consists principally of the glycerol esters of palmitic,  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ , and stearic,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , acids. When these esters are boiled with an alkali solution, they are decomposed like other esters (see Experiment 29, page 137) and converted into glycerol and the sodium salt of the monobasic acid.



Thus, when the glycerol ester of stearic acid,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}$ ,

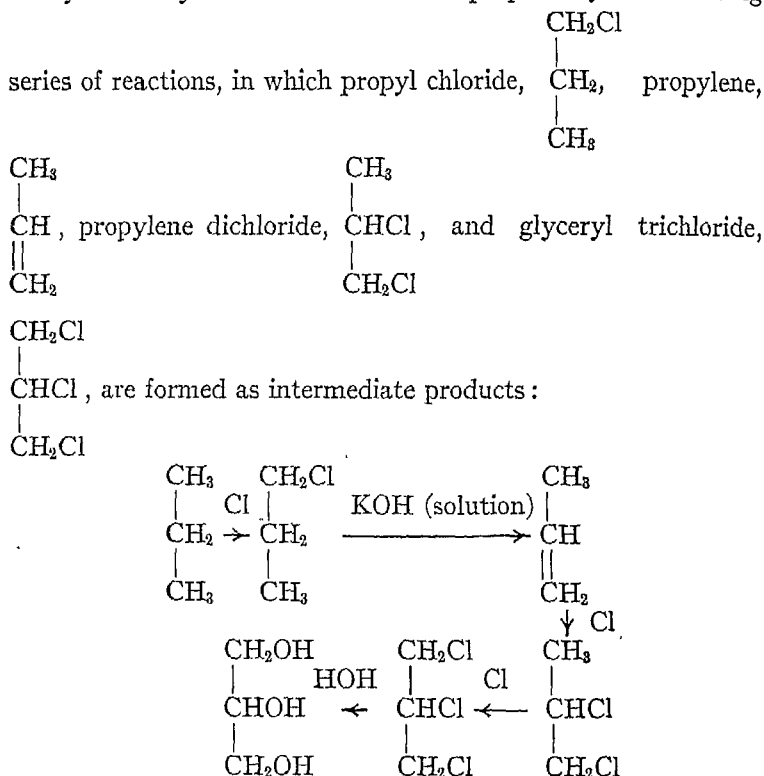


is boiled with sodium hydroxide, it is converted into glycerol and sodium stearate,  $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$ :



Since sodium stearate is a soap, this process, which is called *saponification*, is used in preparing sodium stearate and other soaps. Glycerol is obtained, then, as a by-product in the manufacture of soaps. The glycerol, thus obtained in crude condition, is separated from the soaps and purified by steam distillation, after which it is evaporated to a syrup under reduced pressure.

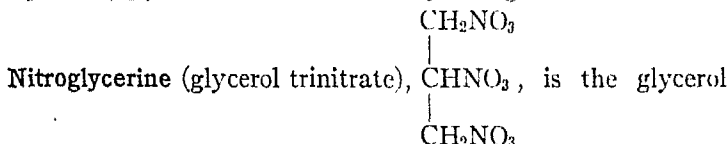
Glycerol may also be obtained from propane by the following



Glycerol is a thick, colorless liquid soluble in water and alcohol. It boils at  $290^\circ$ , has a sweet taste, and is very hygroscopic. It is a good solvent for many substances and finds extensive use in the manufacture of nitroglycerine, in pharmaceutical preparations, and in other lines of industry.

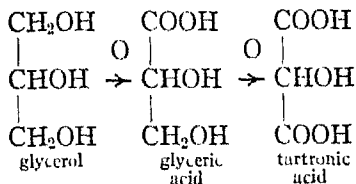


**Derivatives of glycerol.** Glycerol consists of two primary alcohol groups united to a secondary alcohol radical and shows the characteristic reactions of these groups. Like other hydroxyl compounds, glycerol reacts with acids yielding esters.



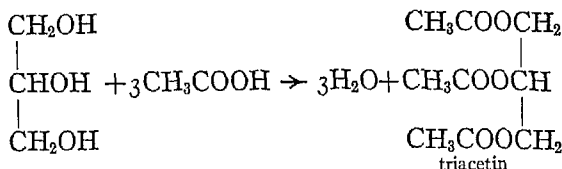
ester of nitric acid. It is prepared by adding glycerol to a mixture of nitric and sulfuric acids; the nitroglycerine separates as a heavy oil. It is very soluble in ether, difficultly soluble in alcohol, and practically insoluble in water. It is a dangerous substance to handle, as it explodes with great violence when subjected to percussion. It is used extensively as an explosive in the form of dynamite, which is a mixture of infusorial earth and nitroglycerine. It is also used as an ingredient in other explosives, such as blasting gelatine, which is a mixture of nitroglycerine and nitrocellulose. Nitroglycerine is the glycerol ester of nitric acid and not a nitro compound.

When glycerol is oxidized under the proper conditions, the primary alcohol groups are converted into carboxyl groups, and it yields glyceric acid, which on further oxidation is converted to tartronic acid:

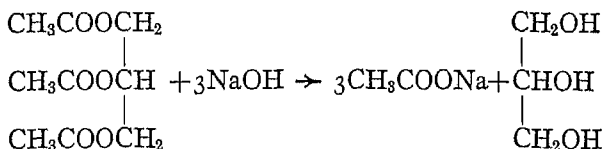


Glyceric acid is hydroxy lactic acid, and tartronic acid is hydroxy malonic acid.

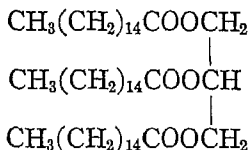
When glycerol is heated with acetic acid, it forms the glycerol ester of acetic acid known as *triacetin*:



In the presence of a smaller amount of acetic acid and at lower temperatures only one, or two, of the hydroxyl groups in glycerol may be acted upon, and consequently compounds such as mon-acetin,  $\text{C}_3\text{H}_5(\text{OH})_2\text{OOCCH}_3$ , and diacetin,  $\text{C}_3\text{H}_5(\text{OH})(\text{OOCCH}_3)_2$ , may be obtained. The same products are obtained more readily by treating glycerol with acetic anhydride. Triacetin when boiled with an alkali is decomposed into glycerol and sodium acetate (see Experiment 29, page 137):



**Fats and soaps.** Fats are the glycerol esters of certain acids, principally the monobasic acids palmitic,  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ , and stearic,  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ , and the unsaturated acid oleic,  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ , together with other monobasic acids such as capric,  $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ , lauric,  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ , myristic,  $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ , etc. The glycerol ester of palmitic acid,



is commonly called *palmitin*, while the glycerol esters of stearic and oleic acids are known as *stearin* and *olein*, respectively. Palmitin and stearin are solids, while olein is a liquid. These esters occur naturally in fats and oils of animal or vegetable

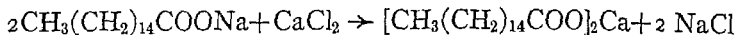
origin. As examples of animal fats may be mentioned lard, beef tallow, and butter. Vegetable fats occur in certain oils such as olive, cottonseed, and palm oil. These oils are obtained by pressing the seeds, or fruit, of certain plants. Butter consists of a mixture of fats, water, and small quantities of casein, milk sugar, and salts. It contains also the glycerol ester of butyric acid.

The glycerol esters which occur in fats are hydrolyzed by water and converted into glycerol and an acid. When boiled with alkalis these glycerol esters are decomposed, yielding glycerol and the alkali salts of the acids, which are soaps. The glycerol ester of lauric acid, for instance, when treated with sodium hydroxide gives glycerol and the sodium salt of lauric acid,  $\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$ , which is a soap (see Experiment 43, on the following page). The process of decomposing these esters by alkalis and obtaining soaps is called *saponification*. The fats which contain these esters are said to be saponified. Soaps, then, are the sodium or potassium salts of the acids palmitic, stearic, oleic, and other acids such as lauric or myristic, which are present in fats as the glycol esters of these acids.

In manufacturing soaps from fats, the fat is boiled with a solution of sodium hydroxide until it is decomposed into glycerol and the sodium salts of the acids present in the fat. A solution of sodium chloride is now added, and the sodium salts of the acids separate out, forming a hard soap, because they are insoluble in a salt solution. If potassium hydroxide is used to saponify the fat, decomposition is effected as in the case of sodium hydroxide, but being somewhat soluble in salt solution the potassium salts form a jelly-like mass known as *soft soap*. The sodium salts of these complex monobasic acids (fatty acids) are known, then, as *hard soaps*, while the potassium salts are called *soft soaps*.

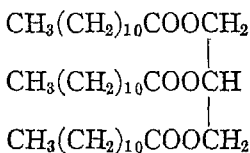
Soap does not dissolve and form a lather with hard water, which contains calcium and magnesium salts, because the soap

reacts with these salts, forming the calcium and magnesium salts of the fatty acids, which are insoluble in water:



Thus the interaction of sodium palmitate,  $\text{CH}_3(\text{CH}_2)_{14}\text{COONa}$ , and calcium chloride gives the insoluble calcium palmitate,  $[\text{CH}_3(\text{CH}_2)_{14}\text{COO}]_2\text{Ca}$ . The cleansing action of soap solutions is due chiefly to the fact that they form emulsions with oily substances, which are easily removed by washing.

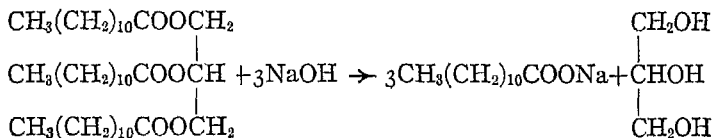
Coconut oil consists principally of the glycerol ester of lauric acid,  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ , and a number of other fats which are the glycerol esters of other fatty acids such as caproic,  $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ , caprylic,  $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ , capric,  $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ , and myristic,  $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ . When these complex esters are saponified, they give reactions similar to the glycerol ester of lauric acid,



and are decomposed, yielding glycerol and a mixture of soaps.

#### EXPERIMENT 43

##### Preparation of soap from coconut oil

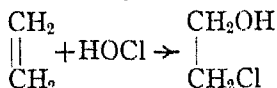


<i>Materials</i>	{	6 grams of sodium hydroxide	
		120 cc. of water	
		30 cc. of coconut oil	
		Methyl benzoate	
		Congo red solution	
		{	Concentrated solution of sodium chloride

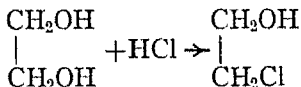
*Procedure.* Prepare a lye solution by dissolving in an evaporating dish 6 grams of sodium hydroxide in 120 cc. of water. Heat the solution until it boils gently. Pour 15 cc. of coconut oil into a dropping funnel, and allow the oil to drop slowly into the hot lye solution, with constant stirring. Now add gradually 15 cc. of the coconut oil in portions of about 3 cc. After the addition of each portion of oil the mixture should be stirred until the oil appears to be dissolved, and then the next portion should be added. The mixture is now allowed to cool to a temperature of about 40°. Add about 3 cc. of some substance like methyl benzoate, which will serve as a perfume. The soap may be dyed red by adding a solution of Congo red (0.2 gram dissolved in 25 cc. of water, or other coloring material may be used). As the soap is insoluble in salt solution, it is precipitated by adding a concentrated solution of sodium chloride until the soap is precipitated completely. Filter the mixture through a cloth (muslin) filter. When the filtration is nearly complete, gather up the ends of the cloth and press out the remaining liquid with your hands. The soap is now pressed into a cake with the aid of a mold. Preserve a specimen.

**Chlorhydrins.** Substances which are obtained from the polyhydroxyl compounds by substituting one or more of the hydroxyl groups by chlorine are called *chlorhydrins*. They contain both chlorine and hydroxyl groups. Thus *ethylene chlorhydrin*,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{Cl} \end{array}$

may be regarded as ethylene glycol,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , in which one hydroxyl group has been substituted by chlorine. It may be prepared by the interaction of ethylene and hypochlorous acid:



It is also obtained by treating ethylene glycol with hydrogen chloride:



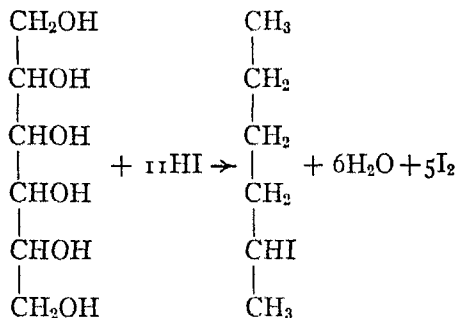
Ethylene chlorhydrin is a sweet liquid which boils at 128°.

When glycerol is heated with hydrogen chloride at  $100^{\circ}$ , it yields alpha chlorhydrin,  $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{Cl}$ , and a small quantity of beta chlorhydrin,  $\text{CH}_2\text{OH}.\text{CHCl}.\text{CH}_2\text{OH}$ . Glycerol yields other chlorhydrins as well, such as alpha dichlorhydrin,  $\text{CH}_2\text{Cl}.\text{CHOH}.\text{CH}_2\text{Cl}$ , and alpha beta dichlorhydrin,  $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}.\text{CH}_2\text{OH}$ .

**Unsaturated compounds related to glycerol.** There are several well-known unsaturated compounds somewhat closely related to glycerol. When glycerol is heated with oxalic acid, the compound monoformin,  $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2.\text{O}.\text{CHO}$ , is obtained (Experiment 23), and as the temperature is increased the monoformin is decomposed, giving *allyl alcohol*,  $\text{CH}_2\text{OH}.\text{CH}=\text{CH}_2$ . Allyl alcohol is a colorless liquid soluble in alcohol, ether, and water, and boils at  $96^{\circ}$ . It is an unsaturated primary alcohol and behaves as an unsaturated compound and as a primary alcohol. When treated with bromine it takes up two atoms of bromine, forming the compound  $\text{CH}_2\text{Br}.\text{CHBr}.\text{CH}_2\text{OH}$ , known as alpha beta dibromhydrin. When oxidized it yields *acrolein*, or acraldehyde,  $\text{CH}_2=\text{CH}.\text{CHO}$ , which on further oxidation is converted into *acrylic acid*,  $\text{CH}_2=\text{CH}.\text{COOH}$ . Acrolein is a colorless liquid boiling at  $52^{\circ}$ . Acrylic acid is a liquid which boils at  $139^{\circ}$  and is a member of the series of unsaturated monobasic acids of which oleic acid is a member. Other unsaturated compounds containing the allyl group ( $\text{CH}_2=\text{CH}.\text{CH}_2$ ), such as allyl iodide,  $\text{CH}_2=\text{CH}.\text{CH}_2\text{I}$ , allyl bromide,  $\text{CH}_2=\text{CH}.\text{CH}_2\text{Br}$ , and allyl sulfide,  $(\text{CH}_2=\text{CH}.\text{CH}_2)_2\text{S}$ , also have been prepared. The latter compound, which is known as *oil of garlic*, occurs in garlic.

**Other polyhydroxyl alcohols.** We have considered polyhydroxyl alcohols such as glycol, which contains two hydroxyl groups, and glycerol, which contains three hydroxyl groups. There are a number of other polyhydroxyl alcohols containing more than three hydroxyl groups. Many of these compounds occur naturally in vegetable substances. Erythritol,  $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{CH}_2\text{OH}$ , is a tetrahydroxyl alcohol which

occurs in certain lichens and seaweeds. Arabitol and xylitol are isomeric pentahydroxyl alcohols which have the formula  $\text{CH}_2\text{OH}(\text{CHOH})_3\text{CH}_2\text{OH}$ . Arabitol may be prepared by reducing arabinose with sodium amalgam, and in a similar manner xylitol may be obtained from xylose. Arabinose and xylose are two simple sugars which are present in various vegetable products such as gum arabic and wood gum. Hexahydroxyl alcohols such as mannitol, sorbitol, and dulcitol occur in the sap of certain trees. They are isomeric compounds and have the formula  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$ . Mannitol is a constituent of manna, which is the dried sap of a tree known as the manna ash. It is a crystalline substance having a sweet taste. When oxidized with nitric acid it yields the sugars mannose and fructose. When reduced with hydrogen iodide it yields hexyl iodide,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHICH}_3$ , which is a derivative of normal hexane:



This reaction indicates that the hexahydroxyl alcohols are derivatives of normal hexane, a fact which accords with their general chemical behavior. When treated with acetic anhydride, mannitol yields a hexacetyl derivative which shows the presence of six hydroxyl groups. These hydroxyl groups must be united to different carbon atoms, because one carbon atom united to more than one hydroxyl group gives an unstable condition.

The formulas of some of the polyhydroxyl compounds we have considered are given on the following page.

## POLYHYDROXYL COMPOUNDS

ETHYLENE GLYCOL	GLYCEROL	ERYTHRITOL	ARABITOL	MANNITOL
CH <sub>2</sub> OH   CH <sub>2</sub> OH	CH <sub>2</sub> OH   CHOH   CH <sub>2</sub> OH	CH <sub>2</sub> OH   CHOH   CHOH   CH <sub>2</sub> OH	CH <sub>2</sub> OH   CHOH   CHOH   CHOH   CH <sub>2</sub> OH	CH <sub>2</sub> OH   CHOH   CHOH   CHOH   CHOH   CH <sub>2</sub> OH

As the number of hydroxyl groups in these polyhydroxyl compounds is increased, the compounds become sweeter in taste. Glycol, glycerol, erythritol, and mannitol are substances having a sweet taste, but each one is sweeter than the one preceding it. This is not surprising when we consider that the hexahydroxyl alcohols are compounds which are closely related to the monosaccharides or simple sugars.

## QUESTIONS

1. What kind of substances are polyhydroxyl compounds?
2. How is ethylene glycol obtained?
3. How is the structure of ethylene glycol determined?
4. Show by outline equations how the structure of ethylene glycol agrees with its chemical behavior.
5. How does glycerol occur naturally?
6. Write the complete structural formulas of ethylene glycol and glycerol. From what hydrocarbons are these substances derived?
7. How is nitroglycerine obtained, and for what purposes is it used?
8. What products are formed by the oxidation of glycerol?
9. Explain, with formulas, what is meant by "fats" and "soaps."
10. What is meant by "saponification"? Give equations.
11. Why is it that soaps do not form a lather with hard water?
12. To what fact is the cleansing action of soap due?
13. Explain, with equations, the preparation of soap from coconut oil.
14. What are chlorhydrins?
15. Write the structural formulas of the following compounds: allyl alcohol; acrolein; acrylic acid; erythritol; mannitol.



## CHAPTER FOURTEEN

### DIBASIC ACIDS

WE have studied monobasic acids such as formic and acetic which contain one carboxyl group. There are a number of acids containing more than one carboxyl group. Those which have two carboxyl groups are known as *dibasic acids*, while those with three carboxyl groups are called *tribasic acids*. The dibasic acids form a homologous series of compounds, the higher members of which exist in isomeric forms. In the following table are given a few of these compounds:

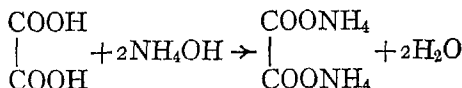
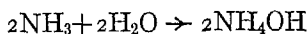
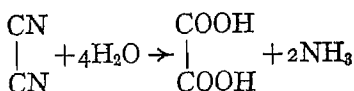
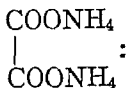
DIBASIC ACIDS

NAME	FORMULA	MELTING POINT, °C.
Oxalic	$\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array}$	189
Malonic	$\text{CH}_2 < \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$	132
Succinic	$\begin{array}{c} \text{CH}_2.\text{COOH} \\   \\ \text{CH}_2.\text{COOH} \end{array}$	182
Glutaric	$\text{CH}_2 < \begin{array}{c} \text{CH}_2.\text{COOH} \\ \text{CH}_2.\text{COOH} \end{array}$	98
Adipic	$\begin{array}{c} \text{CH}_2.\text{CH}_2.\text{COOH} \\   \\ \text{CH}_2.\text{CH}_2.\text{COOH} \end{array}$	153
Pimelic	$\text{CH}_2 < \begin{array}{c} \text{CH}_2.\text{CH}_2.\text{COOH} \\ \text{CH}_2.\text{CH}_2.\text{COOH} \end{array}$	105.5

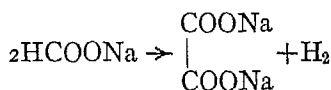
• Oxalic acid,  $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$ , the first of this series of dibasic acids,

is not derived from a hydrocarbon. Since it has the structure of these acids, it is conveniently included in this series of compounds.

It occurs naturally in certain plants, such as rhubarb and sorrel, in the form of its salts, or oxalates, and may be prepared by various methods. When an aqueous solution of cyanogen is allowed to stand, the cyanogen radicals are gradually hydrolyzed to carboxyl groups, and the oxalic acid thus obtained interacts with the ammonia present to form ammonium oxalate,

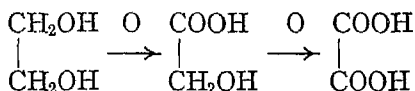


Oxalic acid may be obtained in the form of its sodium salt by heating sodium formate (Experiment 44 *E*) :



Oxalic acid is also obtained by the oxidation of glycol,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ ,

and glycolic acid,  $\text{CH}_2 < \begin{array}{c} \text{OH} \\ \text{COOH} \end{array}$  :

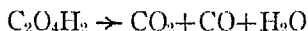


and when sugar, cellulose, and various other organic compounds are oxidized by nitric acid. The commercial preparation of oxalic acid consists in heating sawdust, which contains a considerable quantity of cellulose, with sodium or potassium hydroxide.

Oxalic acid crystallizes from its aqueous solution as colorless crystals containing two molecules of water of crystallization. When heated it loses its water at  $100^{\circ}$ , and on further heating at a temperature of about  $150^{\circ}$  sublimes in slender needles. Oxalic acid and its soluble salts are very poisonous.

*Structure.* The constitution of oxalic acid is determined in accordance with the following facts: It contains two carboxyl groups and is a dibasic acid forming both acid and neutral salts, and the vapor density determined from its neutral esters shows the molecular formula to be  $C_2O_4H_2$ . It may be prepared by oxidizing glycol and glycolic acid, and these reactions show that it probably consists of two carboxyl groups united together.

*Reactions.* When oxalic acid is heated it is decomposed into carbon dioxide, carbon monoxide, and water:

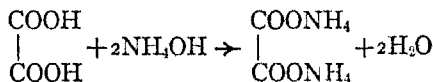


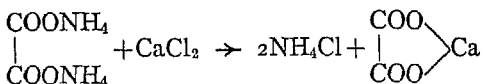
Oxalic acid is easily oxidized by potassium permanganate, manganese dioxide, and other oxidizing agents. It is a very strong organic acid and is used in dyeing and as a reagent in analytical chemistry. There are a number of well-known salts of oxalic acid. These are insoluble or difficultly soluble in water, with the exception of the alkali salts, which are readily soluble. Ammonium oxalate is used to precipitate calcium from solutions in which it is present. The precipitation of the insoluble calcium oxalate serves as a test both for oxalic acid and calcium salts.

#### EXPERIMENT 44

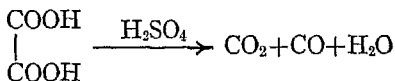
##### Reactions of oxalic acid

A. Neutralize an oxalic acid solution (1:10) with ammonia (1:10), and add a solution of calcium chloride (1:10); a precipitate of white calcium oxalate is obtained. Try the solubility of this precipitate in acetic and hydrochloric acids:

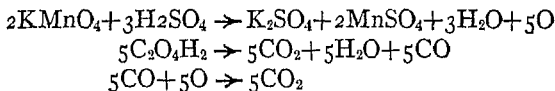




B. Heat in a test tube about 2 grams of oxalic acid with about 5 cc. of concentrated sulfuric acid. How could you test the gases which are evolved?



C. Pour about 2 cc. of an oxalic acid solution (1:10) into a test tube, and add a few drops of a dilute solution of sulfuric acid (1:5). A few drops of a dilute, rose-colored solution of potassium permanganate is now added. The permanganate solution is decolorized immediately:



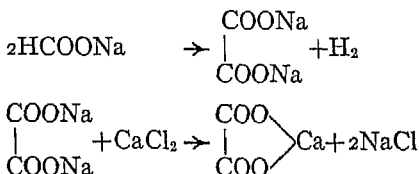
Write these reactions in one equation.

D. Mix about 0.5 gram of oxalic acid with about 0.5 gram of powdered manganese dioxide. Add about 3 cc. of dilute sulfuric acid (1:5). Carbon dioxide is evolved. How could you test it?



Show the exact mechanism of this reaction by writing it in several equations.

E. Heat about 1 gram of dry sodium formate in a test tube and ignite the gas which is evolved. Cool the tube, dissolve the fused mass in water, and add calcium chloride solution (1:10):



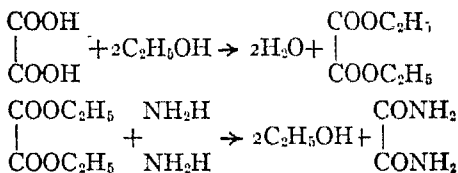
Esters of oxalic acid are prepared by the interaction of oxalic acid and alcohols. **Ethyl oxalate**,  $\text{C}_2\text{O}_4(\text{C}_2\text{H}_5)_2$ , for instance, may be obtained by distilling a mixture of dehydrated oxalic

acid and absolute alcohol in a current of alcohol vapor. The alcohol vapor is passed into the mixture from another flask to remove the water formed as a result of the forward action. The

amide of oxalic acid,  $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{array}$ , which is known as *oxamide*, is prepared as in the case of acetamide by treating an ester of oxalic acid with ammonia.

## EXPERIMENT 45

Preparation of diethyl oxalate,  $\begin{array}{c} \text{COOC}_2\text{H}_5 \\ | \\ \text{COOC}_2\text{H}_5 \end{array}$   
and oxamide,  $\begin{array}{c} \text{CONH}_2 \\ | \\ \text{CONH}_2 \end{array}$



*Materials*  $\left\{ \begin{array}{l} 25 \text{ grams dehydrated oxalic acid} \\ 75 \text{ cc. absolute alcohol} \end{array} \right.$

*Procedure.* Arrange an apparatus as shown in Figure 17. A 200 cc. distilling flask, *A*, is connected to a 200 cc. round flask, *B*, which in turn is connected to a condenser. The dehydrated oxalic acid may be obtained from the stock room or prepared in accordance with the note given at the end of this experiment.

Disconnect the apparatus, which has been previously arranged. Place 25 grams of dehydrated oxalic acid in the round flask, *B*, and add 35 cc. absolute alcohol. Pour into flask *A* 40 cc. of absolute alcohol. Flask *A* is closed with a stopper, through which passes a safety tube dipping into the alcohol. The second flask, *B*, containing the mixture of alcohol and acid, is immersed in an oil bath, *C*, and connected to a condenser. The entire apparatus is now connected as shown in the figure. A thermometer suspended from the iron stand is allowed to dip into the oil bath, *C*.

The oil bath, *C*, is heated gradually to  $100^{\circ}$ . Flask *A* is now heated over a wire asbestos gauze with a small flame until the alcohol boils

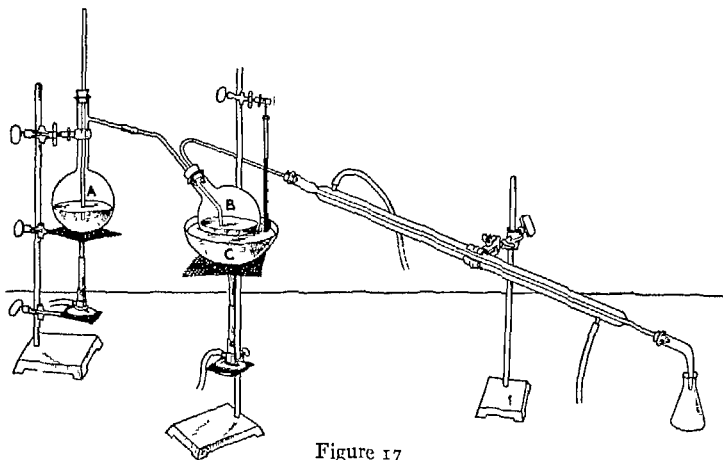


Figure 17

gently. The alcohol vapor from flask *A* is passed into flask *B*. The temperature of the bath *C* is now raised until the thermometer registers  $125^{\circ}$ . The alcohol and oxalic acid in flask *B* react to form ethyl oxalate. A portion of the yield is lost, however, as a mixture of ethyl oxalate and alcohol distils over through the condenser. When all the alcohol has distilled over from flask *A* into flask *B*, discontinue the operation.

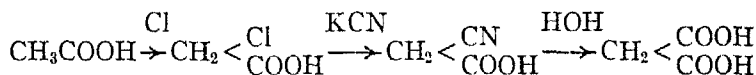
The apparatus is now disconnected. The reaction product in flask *B*, consisting of a mixture of ethyl oxalate and alcohol, is poured into a 300 cc. beaker and allowed to cool. Should a precipitate settle out at this stage, add a small amount of water to dissolve it. The oxamide is precipitated by adding to the ethyl oxalate concentrated ammonia, which should be poured in gradually, as the reaction takes place with some violence. The ammonia should be added until no further precipitate of oxamide is obtained. Now add about 150 cc. of water, filter, and wash with water. Calculate the yield and preserve a specimen.

Ethyl oxalate is a colorless liquid which boils at  $186^{\circ}$ . Methyl oxalate prepared in a similar manner is obtained as colorless crystals which melt at  $54^{\circ}$ . Oxamide is a white crystalline solid. When heated it is partly sublimed, but the greater portion of it is decomposed into cyanogen and water.

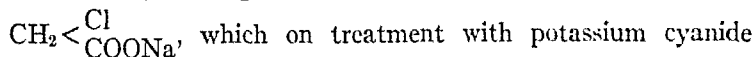
A. Boil in a test tube about 1 gram of oxamide with a solution of potassium hydroxide (1 : 10), and note the odor of the gas evolved. How would acetamide behave when treated in a similar manner?

NOTE. Preparation of dehydrated oxalic acid. A sufficient quantity of powdered, crystallized oxalic acid is placed in an evaporating dish and heated in an air bath at 100°. A cork stopper through which a thermometer has been passed is placed in the opening at the top of the air bath and the thermometer so adjusted that the mercury bulb is at the same level in the bath as the dish containing the oxalic acid. Occasionally, with the aid of a pair of crucible tongs, the dish should be removed from the bath, the material stirred and powdered, and the dish placed again in the bath. After the material has been heated and occasionally stirred for about an hour, it will be mostly dehydrated. The dish is now removed from the bath, allowed to cool somewhat, and the contents scraped out into a mortar, powdered rapidly, and placed in a bottle, which is stoppered and set aside until required.

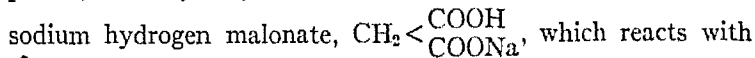
**Malonic acid**,  $\text{CH}_2 < \begin{smallmatrix} \text{COOH} \\ \text{COOH} \end{smallmatrix}$ , the second member of this series of dibasic acids, may be regarded as the dicarboxyl derivative of methane or the monocarboxyl derivative of acetic acid. It may be prepared from acetic acid by a series of reactions in which chlor and cyan acetic acids are formed as intermediate products, as shown by the following outline equations:



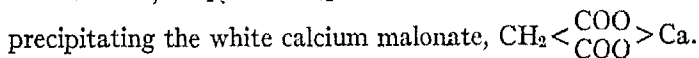
Malonic acid is easily prepared in the laboratory from monochlor acetic acid. This substance is neutralized with sodium bicarbonate, forming the sodium salt of monochlor acetic acid,



yields sodium cyan acetate,  $\text{CH}_2 < \begin{smallmatrix} \text{CN} \\ \text{COONa} \end{smallmatrix}$ . The latter compound, when hydrolyzed with sodium hydroxide solution, yields



the alkali present in the solution, forming the disodium salt of malonic acid,  $\text{CH}_2(\text{COONa})_2$ . This reacts with calcium chloride,

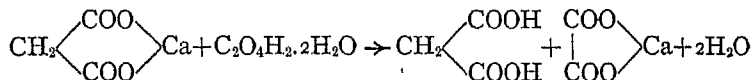
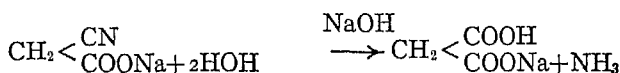
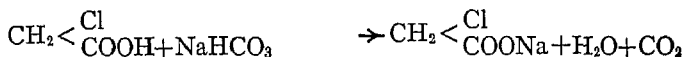


Malonic acid is obtained from the latter salt by treating it with a solution containing the calculated quantity of crystallized oxalic acid. Thus, malonic acid is obtained from monochlor acetic acid by a series of reactions in which calcium malonate is separated as an intermediate product.

## EXPERIMENT 46

Preparation of malonic acid,  $\text{H}-\overset{\text{H}}{\underset{\text{COOH}}{\text{C}}}-\text{COOH}$ , or  $\text{CH}_2(\text{COOH})_2$

and calcium malonate,  $\text{CH}_2<\overset{\text{COO}}{\underset{\text{COO}}{\text{C}}}>\text{Ca}$



*Materials* { Solution of 25 grams of monochlor acetic acid dissolved in 50 cc. of water  
23 grams of sodium bicarbonate  
20 grams of potassium cyanide  
Solution of 20 grams of sodium hydroxide dissolved in 50 cc. of water  
Solution of 38 grams of calcium chloride dissolved in 60 cc. of water  
Crystallized oxalic acid (quantity calculated)

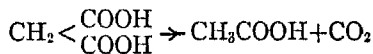
*Procedure.* Place 25 grams of monochlor acetic acid in a liter porcelain evaporating dish, under a hood. (*Caution!* Do not get the



monochlor acetic acid on your hands.) The acid is dissolved in 50 cc. of water and neutralized by adding gradually, with constant stirring, 23 grams of powdered sodium hydrogen carbonate ( $\text{NaHCO}_3$ ). Heat the mixture to a temperature of about  $55^\circ$  (not above  $60^\circ$ ), and stir until no more carbon dioxide is evolved. 20 grams of powdered potassium cyanide are now added gradually, with stirring. Do not breathe any of the escaping vapors, as they may contain poisonous hydrogen cyanide. After the cyanide has been added, the mixture is warmed gently until the reaction, which takes place with considerable evolution of heat, is complete. The mixture is now heated 0.5 hour longer at a temperature of about  $40^\circ$ , after which is added a solution of 20 grams of sodium hydroxide dissolved in 50 cc. of water. The alkaline liquid is boiled until no more ammonia is given off. The solution is now neutralized with a solution of dilute hydrogen chloride (1 : 5), and the malonic acid precipitated as the calcium salt by adding a solution of 38 grams of calcium chloride dissolved in 60 cc. of water. The calcium malonate is filtered off, washed with cold water, and dried in an air bath heated to  $100^\circ$ . Weigh the product obtained, calculate the yield, and preserve a specimen.

To convert calcium malonate into malonic acid, treat a weighed quantity of the dry calcium malonate with a solution of oxalic acid containing the calculated amount of crystallized oxalic acid. The mixture is heated a short time to digest the precipitated calcium oxalate, filtered, and the filtrate evaporated on a water bath. Preserve a specimen of malonic acid. Malonic acid forms colorless crystals which melt at  $132^\circ$  and are very soluble in water.

A. Heat about 1 gram of malonic acid in a test tube, and test the gas evolved and the liquid which remains:

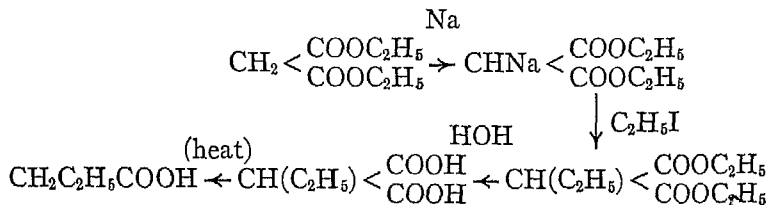


When an acid, such as malonic acid, which contains two carboxyl groups united to one carbon atom, is heated, it frequently decomposes, giving a monobasic acid. The decomposition is important, as it enables us to prepare monobasic acids from dibasic acids.

The structure of malonic acid is determined by the manner in which it decomposes when heated and by the fact that malonic

acid can be prepared synthetically from acetic acid through the cyanide reaction.

**Malonic acid synthesis.** The diethyl ester of malonic acid,  $\text{CH}_2 < \begin{smallmatrix} \text{COOC}_2\text{H}_5 \\ \text{COOC}_2\text{H}_5 \end{smallmatrix}$ , is a liquid which boils at  $198^\circ$ . It is an important reagent which may be used to prepare alkyl-substituted monobasic or dibasic acids. The preparation of these compounds depends upon the fact that malonic acid is easily decomposed into acetic acid and carbon dioxide, and also that the hydrogen atoms in the methylene group of the diethyl ester are replaceable by alkyl radicals. When the ester is treated with sodium, or sodium ethoxide, hydrogen is evolved and compounds which appear to be the mono sodium,  $\text{CHNa}(\text{COOC}_2\text{H}_5)_2$ , or disodium derivative of the ester,  $\text{C}(\text{Na}_2)(\text{COOC}_2\text{H}_5)_2$ , are obtained, depending upon the proportion of sodium used. By treating these sodium compounds with alkyl halides, such as ethyl iodide, the sodium is replaced by the alkyl radical, giving alkyl-substituted esters,  $\text{CH}(\text{C}_2\text{H}_5) < \begin{smallmatrix} \text{COOC}_2\text{H}_5 \\ \text{COOC}_2\text{H}_5 \end{smallmatrix}$ , which when hydrolyzed give the alkyl-substituted acids,  $\text{CH}(\text{C}_2\text{H}_5) < \begin{smallmatrix} \text{COOH} \\ \text{COOH} \end{smallmatrix}$ . When the latter compounds are heated, carbon dioxide is evolved, yielding the alkyl-substituted monobasic acids,  $\text{CH}_2 < \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{COOH} \end{smallmatrix}$ . These transformations are indicated in the following outline reactions:

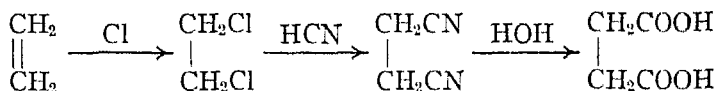


Thus ethyl acetic acid, or normal butyric acid,  $\text{CH}_2 < \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{COOH} \end{smallmatrix}$ , may be prepared in accordance with the reactions above. This

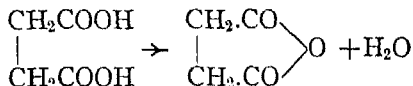
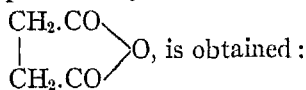
method of preparing alkyl-substituted acids is known as the *malonic acid synthesis*.

Succinic acid,  $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$  (normal, or ethylene succinic acid),

is a colorless crystalline substance which melts at  $185^\circ$  with partial decomposition. It occurs in certain plants and is obtained by distilling amber (succinum). It is one of the products formed by oxidizing certain monobasic acids. It may be prepared synthetically in the laboratory from ethylene by a series of reactions in which ethylene dichloride and ethylene dicyanide are intermediate products:



When distilled alone or with dehydrating agents such as phosphorus oxychloride, it loses water, and succinic anhydride,



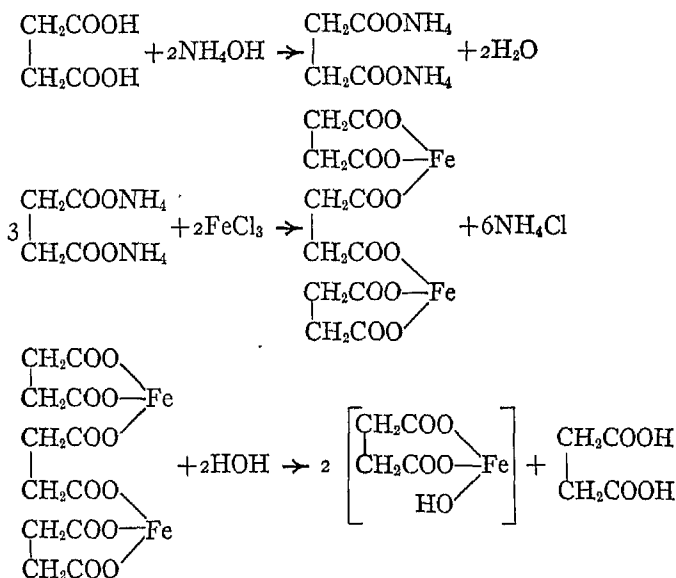
The anhydride is a colorless, crystalline substance melting at  $120^\circ$ . In general, it resembles the anhydrides of other acids. When boiled with water it is converted into succinic acid. The formation of anhydrides is often characteristic of acids containing two carboxyl groups united to different carbon atoms.

**Derivatives of succinic acid.** Succinic acid is a dibasic acid and yields derivatives similar to those obtained from oxalic, malonic, and other dibasic acids. The basic succinates of aluminium and iron are insoluble in water, and succinic acid may therefore be used for separating quantitatively iron and aluminium from manganese, nickel, cobalt, and zinc. Basic

ferric succinate,  $\begin{array}{c} \text{CH}_2\text{COO} \\ | \\ \text{CH}_2\text{COO} \end{array} \text{Fe(OH)}$ , is obtained as a brown gelatinous precipitate by treating a neutral solution of a succinate with a solution of a ferric salt.

## EXPERIMENT 47

## Separation of iron and zinc by succinic acid

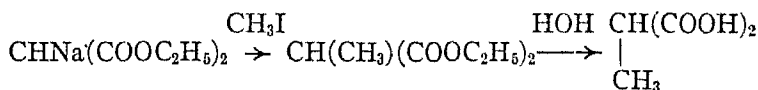


*Materials*  $\left\{ \begin{array}{l} 1 \text{ gram ethylene succinic acid} \\ \text{Solution of ferric chloride (1:10)} \\ \text{Solution of zinc chloride (1:10)} \end{array} \right.$

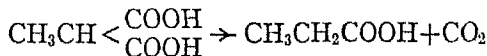
*Procedure.* Dissolve 1 gram of ethylene succinic acid in water. Neutralize the solution with ammonia. This may be accomplished easily by making the solution slightly alkaline and then boiling off the excess of ammonia until the solution shows a neutral reaction. To this neutral solution of ammonium succinate add 2 cc. of a solution of ferric chloride (1:10) and also 2 cc. of a solution of zinc chloride (1:10). A brownish-red precipitate of basic ferric succinate,

$\begin{array}{c} \text{CH}_2\text{COO} \\ | \\ \text{CH}_2\text{COO} \end{array} \rangle \text{Fe(OH)}$ , is obtained. Boil, filter, and divide the filtrate into three portions. Test one portion of the filtrate for iron with potassium ferrocyanide solution, which precipitates Prussian blue,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , if ferric salts are present, and another portion with ammonium sulfide, which precipitates white zinc sulfide, if zinc salts are present. Test another portion of the filtrate and ascertain if it has an acid reaction. Aluminium salts when treated with a neutral solution of ammonium succinate behave in a similar manner.

Isosuccinic acid,  $\begin{array}{c} \text{CH} < \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array} \\ | \\ \text{CH}_3 \end{array}$  (ethylidene succinic acid, or methyl malonic acid), is an isomer of succinic acid. It may be prepared synthetically by the malonic acid synthesis:



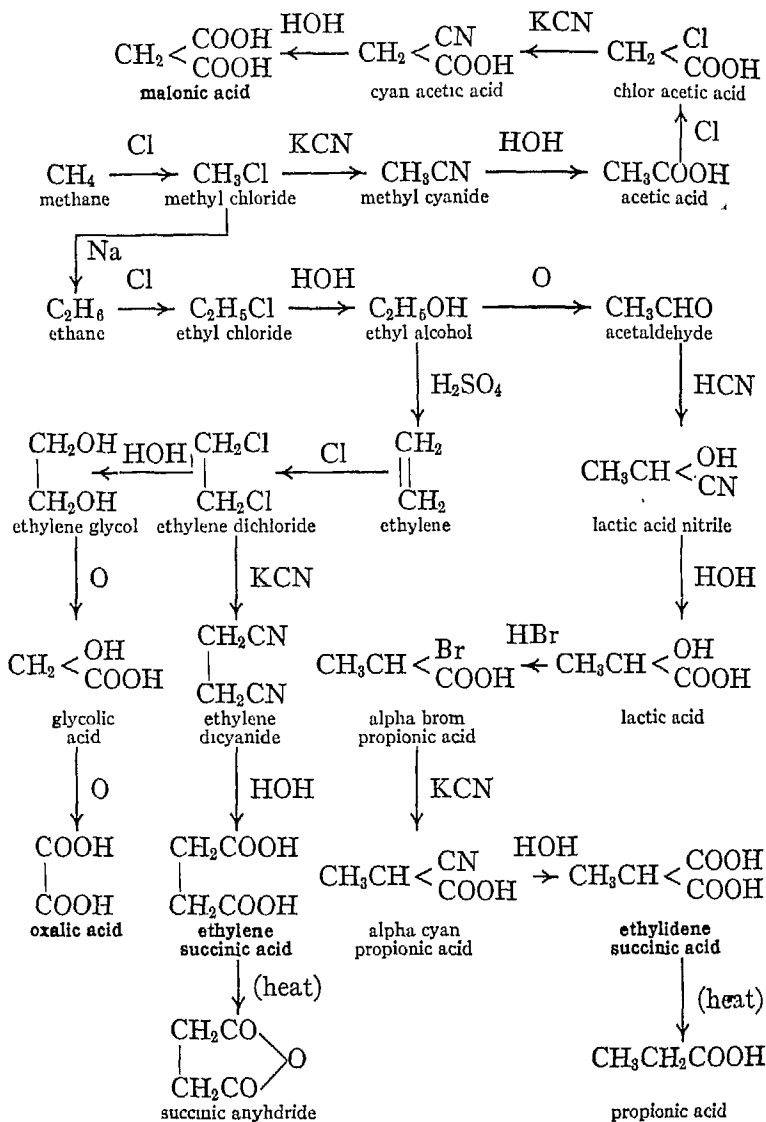
It is a crystalline substance melting at  $130^\circ$ . It contains two carboxyl groups united to one carbon atom, and when heated behaves like malonic acid and is converted into carbon dioxide and the monobasic propionic acid:



The higher members of this series of dibasic acids have a general chemical behavior similar to the lower members.

Tribasic acids such as normal tricarballic acid,  $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CHCOOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ , contain three carboxyl groups. Tricarballic acid is a crystalline substance melting at  $163^\circ$ . Citric acid,  $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{C}(\text{OH})\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ , is the

## DIBASIC ACIDS



monohydroxyl derivative of tricarballic acid and occurs in certain fruit juices. Lemon juice contains a considerable quantity of citric acid, while other fruits, such as gooseberries and raspberries, contain small quantities of the acid. It is prepared commercially from lemon juice, which is first boiled to precipitate albuminous matter, after which it is neutralized with calcium carbonate and the precipitated calcium citrate filtered off. The calcium salt is then treated with the required amount of dilute sulfuric acid, and the solution filtered to eliminate insoluble calcium sulfate, after which the filtrate is allowed to crystallize.

## QUESTIONS

1. What are dibasic acids?
2. How is oxalic acid obtained and tested?
3. Explain, with equations, the laboratory preparation of diethyl oxalate and oxamide.
4. Show by outline equations how malonic acid may be obtained from acetic acid.
5. Explain, with equations, the laboratory preparation of malonic acid and calcium malonate.
6. Explain how alkyl-substituted acids may be obtained by the malonic acid synthesis.
7. Outline the equations indicated: ethylene  $\rightarrow$  succinic anhydride.
8. Explain the succinic acid separation of iron and aluminium from manganese, nickel, cobalt, and zinc.
9. Outline the equations indicated:
  - a. methane  $\rightarrow$  malonic acid.
  - b. methane  $\rightarrow$  ethylene glycol  $\rightarrow$  oxalic acid.
10. Write the complete structural formulas of oxalic, malonic, and ethylene succinic acids.
11. From what hydrocarbons are malonic and ethylene succinic acids derived?

## CHAPTER FIFTEEN

### HYDROXY ACIDS AND STEREOCHEMISTRY

WE have studied compounds such as methyl alcohol,  $\text{CH}_3\text{OH}$ , which contains one hydroxyl group, and acetic acid,  $\text{CH}_3\text{COOH}$ , which contains one carboxyl group. Now there are a number of compounds such as glycolic acid,  $\text{CH}_2 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ , which contain both hydroxyl and carboxyl groups. These mixed compounds have both acid and alcohol properties, but since the acid properties are more prominent they are known as *hydroxy acids*. These hydroxy acids are substituted monobasic acids. A few of the simpler hydroxy acids and the monobasic acids from which they are derived are given below :

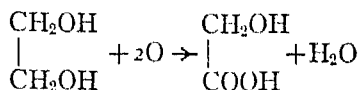
MONOBASIC ACIDS	HYDROXY ACIDS
$\text{HCOOH}$ formic	$\text{HO} \cdot \text{COOH}$ or $\text{H}_2\text{CO}_3$ carbonic
$\text{CH}_3\text{COOH}$ acetic	$\text{CH}_2 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ glycolic
$\begin{array}{c} \text{CH}_2\text{COOH} \\   \\ \text{CH}_3 \\ \text{propionic} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{COOH} \\ \text{hydracrylic} \end{array}$
	$\begin{array}{c} \text{CH} < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix} \\   \\ \text{CH}_3 \\ \text{inactive lactic} \end{array}$

The simplest hydroxy acid is the unstable carbonic acid, which may be regarded as the hydroxy derivative of formic acid.

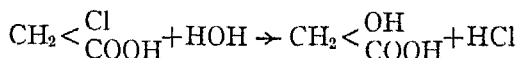
Glycolic acid (hydroxy acetic acid),  $\text{CH}_2 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ , is a <sup>\*</sup>crystalline substance which occurs in unripe grapes, and melts at  $80^\circ$ . It can be obtained by various methods, one of which is the oxida-



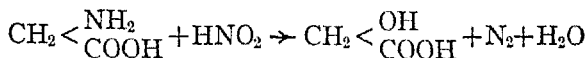
tion of glycol,  $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$ , and hence it is called glycolic acid :



Glycolic acid, like other hydroxy acids, is also obtained by hydrolyzing a halogen-substituted acid :



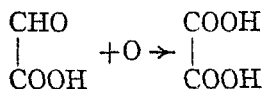
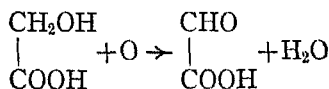
and by the interaction of an amino-substituted acid and nitrous acid :



Glycolic acid contains one carboxyl group united to a primary alcohol group. It therefore gives reactions characteristic of primary alcohols and of acids. When oxidized, the primary alcohol group ( $\text{CH}_2\text{OH}$ ) is converted into the aldehyde group

( $\text{CHO}$ ), giving the compound glyoxylic acid,  $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array}$ , which on

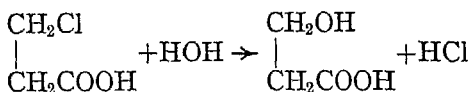
further oxidation is converted into oxalic acid,  $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$  :



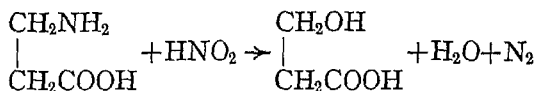
It interacts with metallic hydroxides, giving salts such as the potassium salt of glycolic acid,  $\text{CH}_2 < \begin{array}{c} \text{OH} \\ \text{COOK} \end{array}$ , and with alcohols, yielding esters such as the ethyl ester of glycolic acid,  $\text{CH}_2 < \begin{array}{c} \text{OH} \\ \text{COOC}_2\text{H}_5 \end{array}$ .

**Hydroxy propionic acids.** Propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , yields two isomeric monohydroxy derivatives. These are *hydracrylic acid*,  $\text{CH}_2(\text{OH})\text{CH}_2\text{COOH}$ , which is beta hydroxy propionic acid, and inactive *lactic acid*,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , which is alpha hydroxy propionic acid.

Hydracrylic acid may be obtained by hydrolyzing beta chlor propionic acid.



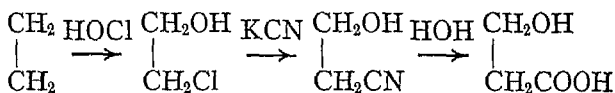
or by the interaction of beta amino propionic acid and nitrous acid,



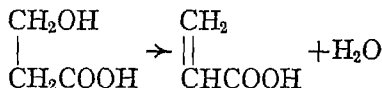
It may be prepared from ethylene by a series of reactions in which

ethylene chlorhydrine,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{Cl} \end{array}$ , and ethylene cyanhydrine,

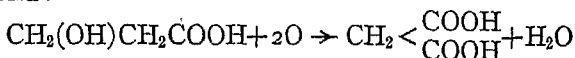
$\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{CN} \end{array}$ , are formed as intermediate products:



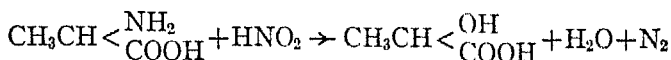
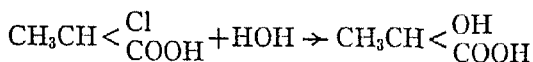
Hydracrylic acid is a thick, sour liquid which decomposes when distilled, forming acrylic acid,  $\text{CH}_2=\text{CHCOOH}$ :



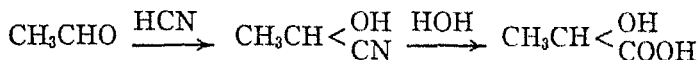
It contains one primary alcohol group, which when oxidized with chromic acid is converted into a carboxyl group, forming malonic acid:



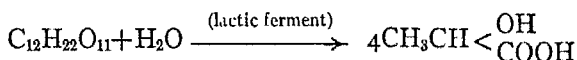
Inactive lactic acid may be prepared by hydrolyzing alpha chlor propionic acid and by heating alpha amino propionic acid with nitrous acid :



It may also be prepared synthetically from acetaldehyde :



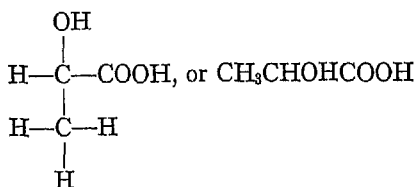
This synthesis shows that inactive lactic acid contains the hydroxyl and carboxyl groups united to the same carbon atom and hence it has the structure which has been assigned to it. Inactive lactic acid is also formed naturally during the lactic fermentation of sugars and is present in sour milk. When milk is exposed to the air for some length of time, it gradually turns sour. This is due to the fact that the milk sugar, or lactose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , which is a constituent of milk, is converted into lactic acid by an organism known as the *lactic ferment* which is present in the air :



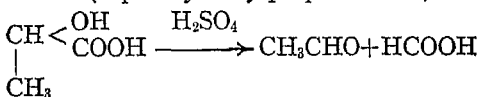
Inactive lactic acid is a thick, colorless liquid which is soluble in water, alcohol, and ether. It is manufactured commercially by the fermentation of sugar and is used in dyeing and calico printing. The antimony salt of inactive lactic acid is used as a mordant. When heated with dilute sulfuric acid, inactive lactic acid is decomposed into acetaldehyde and formic acid.

## EXPERIMENT 48

## Decomposition of inactive lactic acid



(Alpha hydroxy propionic acid)



*Materials* { Dilute sulfuric acid solution  
 12 cc. inactive lactic acid

*Procedure.* Prepare a dilute solution of sulfuric acid by adding 6 cc. of concentrated sulfuric acid to about 10 cc. of water and diluting the mixture to a volume of 20 cc. Pour this solution into a 100 cc. distilling flask, and add 12 cc. of inactive lactic acid. Distil the mixture until about half of it has passed over into the receiver. Divide the distillate into two portions. Test one portion for acetaldehyde, using the silver mirror test (Experiment 20), and test the other portion for formic acid by the reduction of mercuric chloride solution (Experiment 24 F).

As we have already stated, propionic acid yields two monohydroxy derivatives, which are hydracrylic acid (beta hydroxy propionic acid) and inactive lactic acid (alpha hydroxy propionic acid). In addition to these two monohydroxy derivatives of propionic acid there are two other varieties of alpha hydroxy propionic acid, known as *d*-lactic and *l*-lactic acids. We have, then, three varieties of alpha hydroxy propionic acid (lactic acids):

I. **Inactive lactic acid** (*i*-lactic) is the ordinary, or common, variety of the lactic acids. It is called "inactive" because it is "optically inactive"; that is, a solution of it does not affect polarized light.

II. **Dextro lactic acid** (*d*-lactic), or sarco lactic acid, is a constituent of beef extract, from which it may be obtained. It is called "dextro" because it is optically active and rotates the plane of polarized light to the right (*dextro*).

III. **Levo lactic acid** (*l*-lactic) is obtained by fermenting cane sugar with the levo lactic acid ferment (*Bacillus acidi levolacti*). It is optically active, but unlike the *d*-lactic acid rotates the plane of polarized light to the left (*levo*).

Since these lactic acids have the same structural formulas, it is obvious that we cannot distinguish them by our ordinary chemical formulas. They present a different kind of isomerism from that which we have already studied, and we must find some other means of designating these substances. We will first ascertain what is meant by the terms "optically active," "dextro," and "levo," after which we will consider the method of separating an inactive compound into its active isomers, and also the theory of stereochemistry, which explains the chemistry of optically active compounds such as the isomeric lactic acids.

**Optical activity.** Light travels in straight lines and vibrates in all directions perpendicular to the direction of propagation. Plane polarized light is that which travels in a straight line and vibrates in only one plane perpendicular to the direction of propagation. Polarized light is obtained by passing a beam of white light, or better, of monochromatic light such as a sodium light, through a Nicol's prism. A beam of polarized light emerging from a Nicol's prism vibrates then, in only one plane, which is called the *plane of polarization*. If this beam of polarized light is now passed through a solution containing an optically active substance, the plane of polarized light is turned or rotated a certain amount to the right or left. Substances such as the lactic acids, malic, tartaric acids, and the sugars have the power of rotating the plane of polarization and are known as *optically active substances*.

The instrument used for measuring the rotation of polarized

light is known as a *polariscope*, or *polarimeter*. Although there are various kinds of polariscopes, they all consist essentially of two Nicol's prisms. Light from a certain source, such as an incandescent electric light, or monochromatic light obtained by heating fused sodium chloride, is allowed to pass through the first Nicol's prism (polarizer). The polarized light emerging from the polarizer is then passed into a second Nicol's prism (analyzer), which is so turned that the light emerging from the analyzer presents a uniform field to the eye. If the instrument is adjusted properly, the scale now indicates a zero reading. A glass tube which contains a solution of some optically active substance to be investigated is now placed between the two Nicol's prisms in the path of the polarized light. The plane of polarization is rotated, with the result that the field of the analyzer is no longer uniform in color. In order to make the field of the analyzer again uniform in color, it is necessary to rotate the analyzer a certain number of degrees to the right or left. The number of degrees through which the analyzer must be rotated is now read on the scale. This reading represents the number of degrees which the plane of polarization has been turned by the layer of the solution. The mechanism of polariscopes has been improved considerably in recent years, but it would lead too far into a discussion of such instruments to describe the more recent designs.

The rotation of the plane of polarization by a solution of an optically active substance depends chiefly upon the chemical nature of the substance. It depends also upon the length of the layer of liquid through which the polarized light passes, upon the wave length of light employed, and upon the temperature and concentration of the solution. Thus rotation is therefore dependent upon various factors, and in stating results it is customary to state the exact experimental conditions. The specific rotatory power of a substance is denoted by the symbol  $[\alpha]_D^t$

and means the specific rotation of the substance as determined with sodium light at  $t^\circ$ . The standard temperature for measurement is  $20^\circ$ . The standard length of tube is 2 decimeters (20 centimeters) and is represented by ( $l$ ). In working with solutions of optically active substances which are very dilute or unusually concentrated, better results are frequently obtained by using tubes which are shorter or longer than the normal length. The reading obtained with tubes of abnormal length must, of course, be referred to the normal length of 20 centimeters. Thus if a tube 10 centimeters in length is employed, the reading must be multiplied by 2 in order to obtain the reading of the standard tube. The concentration is frequently expressed as the number of grams of active substance per cubic centimeter and is represented by ( $d$ ). The actual rotation of the solution in degrees as indicated by the polariscope scale is represented by ( $a$ ). The formula for determining the specific rotation is, then :

$$[\alpha]_D^t = \frac{a}{ld}$$

The following experiment shows how this formula may be applied in determining the specific rotation of an optically active substance such as *d*-lactic acid. The polariscope was adjusted to the zero reading, which gave a field uniform in color. A solution having a volume of 25 cubic centimeters and containing 3.5 grams of *d*-lactic acid was now prepared at  $15^\circ$ . A 2-decimeter tube was now filled with the solution of *d*-lactic acid and placed in the polariscope. Observation showed that the field of the analyzer was no longer uniform in color, and in order to obtain again a uniform field the analyzer had to be rotated  $+0.95^\circ$ . The specific rotation was calculated in accordance with the formula above:

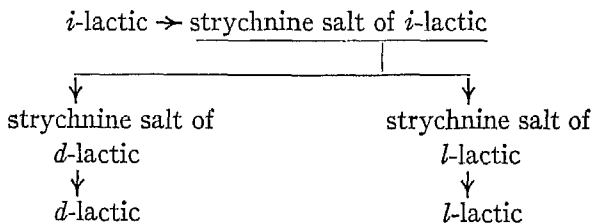
$$[\alpha]_D^{15} = \frac{+0.95}{2 \times \frac{3.5}{25}} = +3.4^\circ$$

In order to make comparisons between the optical rotation of different optically active substances, the term *molecular rotation* is used and is denoted by the symbol  $[M]_D^t$ . The molecular rotation is expressed by multiplying the specific rotation by the molecular weight ( $M$ ) of the substance and dividing the product by 100:

$$[M]_D^t = \frac{[\alpha]_D^t \times M}{100}$$

The polarization of cane sugar solutions is determined with a special kind of polariscope known as a *saccharimeter*. This instrument will be described later (page 261).

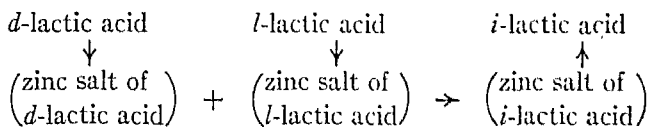
**Separation of an inactive compound into optically active isomers.** The strychnine salt of *l*-lactic acid is less soluble than the strychnine salt of *d*-lactic. When the strychnine salt of *i*-lactic acid is allowed to crystallize, the crystals, which appear first, consist of the strychnine salt of *l*-lactic acid, while the more soluble salt remaining in solution and which is obtained on further crystallization consists of the strychnine salt of *d*-lactic acid. *d*- and *l*-lactic acids may be obtained from the corresponding strychnine salts of these acids. Thus *i*-lactic may be split up into *d*- and *l*-lactic acids:



Conversely, *i*-lactic may be obtained by combining *d*- and *l*-lactic acids through the zinc salts of these acids. The zinc salt of *i*-lactic is less soluble than the zinc salts of *d*- and *l*-lactic acids; hence, when the zinc salts of *d*- and *l*-lactic acids are mixed in



equal proportions, the less soluble zinc salt of *i*-lactic acid crystallizes out and from this *i*-lactic may be obtained :



*d*-lactic acid may also be prepared from the ammonium salt of *i*-lactic by means of a mold known as *Penicillium glaucum*. When this mold is allowed to grow in a solution of the ammonium salt of inactive lactic acid, it destroys the ammonium salt of levo lactic acid by using it as food and leaves the ammonium salt of dextro lactic acid.

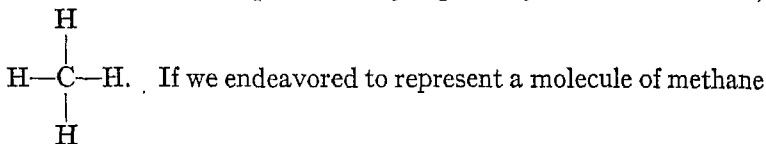
Since the *d*- and *l*-lactic acids may be combined in molecular proportions to produce *i*-lactic acid, and the *i*-lactic may again be split up into the *d*- and *l*-lactic acids, it would seem probable that the *i*-lactic consists simply of an equal number of molecules of *d*- and *l*-lactic acids. If this is true, it would explain why *i*-lactic acid is optically inactive. Suppose a molecule of *i*-lactic acid consists of one molecule of *d*-lactic combined with one molecule of *l*-lactic. The dextro rotation of the molecule of *d*-lactic would neutralize the levo rotation of the molecule of *l*-lactic, and consequently the molecule of *i*-lactic would be inactive. The inactivity in such a case may accordingly be explained as due to external compensation, and an inactive compound such as *i*-lactic acid may be regarded as a (*d*+*l*) compound; that is, an inactive compound is a mixture consisting of an equal number of molecules of the dextro and levo compounds.

**Stereochemistry.** As we have previously explained, there are three isomeric alpha hydroxy propionic acids, which are *i*-lactic, *d*-lactic, and *l*-lactic acids. These three have the same general chemical behavior and therefore the same structural formula,

$\text{CH}_3\text{CH} < \begin{array}{c} \text{OH} \\ \text{COOH} \end{array}$ . It is obvious that our usual methods of designating compounds by means of structural formulas which repre-

sent the chemical behavior of a compound do not enable us to distinguish optically active substances such as the lactic acids. The theory of stereochemistry, which was worked out independently by the two celebrated investigators, Van't Hoff and Le Bel, explains in a satisfactory manner the chemistry of these isomeric optically active compounds and enables us to distinguish them.

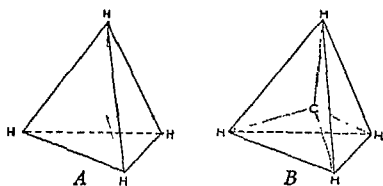
The theory of stereochemistry is based upon the fact that a molecule of a compound may be represented as a solid figure which exists in three dimensions of space (chemistry in space). Let us consider the simple substance methane,  $\text{CH}_4$ . In discussing the chemistry of methane it was pointed out that methane yields no isomeric monosubstitution products; that is, there are no two compounds having a molecular formula such as  $\text{CH}_3\text{Cl}$ , but different in their chemical behavior. In view of this fact we conclude that all the hydrogen atoms in methane bear the same relation to the molecule, and accordingly the molecule of methane is represented by a plane symmetrical formula,



by a solid figure existing in three dimensions of space, we should find that the solid tetrahedron having the carbon atom at the

center and the four hydrogen atoms at the four solid corners is the only solid figure which expresses adequately the symmetrical structure of methane.

In Figure 18 two diagrams are given showing a molecule of methane represented by a

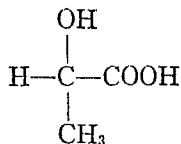


Methane  
Figure 18

solid tetrahedron. Figure 18 A shows an external view of the solid tetrahedron, while Figure 18 B gives an internal view showing

the central carbon atom connected to each of the hydrogen atoms at the four solid corners.

**Asymmetric carbon atom.** The lactic acids contain one carbon atom united to one atom of hydrogen, and to the hydroxyl, carboxyl, and methyl groups — that is, one carbon atom united to four different groups:



A carbon atom united to four different groups is known as an *asymmetric carbon atom*, and a molecule of a compound containing an asymmetric carbon atom has an asymmetrical structure. The active lactic acids may be considered as derived from methane by substituting for three hydrogen atoms the hydroxyl, carboxyl, and methyl groups.

**Stereochemical formulas.** If we regard the active lactic acids as existing in three dimensions of space, it is evident that each of them, like methane, could be represented by a tetrahedron with the carbon atom at the center and the groups in combination with it at the four solid angles. When the molecule of a compound, such as one of the active lactic acids, which contains an asymmetric carbon atom is represented by a solid tetrahedron, there are two possible arrangements of the groups around the central carbon atom (Fig. 19).

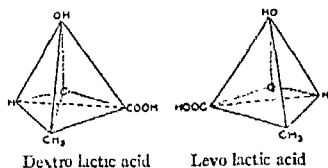


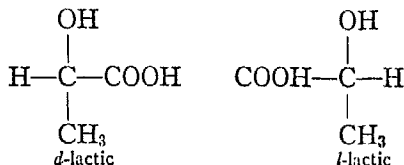
Figure 19

As shown by the solid formulas above, the four groups are connected to the central carbon atom, giving structures which are identical, but the solid formulas themselves are not identical. One of these solid formulas, which we may call *dextro lactic acid*, is the mirror image of the other, which represents *levo lactic*

acid. That is, if the solid formula representing levo lactic acid is held before a mirror, the image observed is identical with the solid formula of dextro lactic acid. These two tetrahedra represent right-handed and left-handed forms, and if one rotates the plane of polarization to the right the other rotates to the left. All optically active carbon compounds contain an asymmetric carbon atom — that is, one carbon atom united to four different groups. According to the theory of stereochemistry, this fact must be true because it is necessary that all the atoms or groups which are combined with the central carbon atom should be different. If any two of the atoms or groups which are combined with the central carbon atom are the same, it is impossible to have two tetrahedra one of which is the mirror image of the other.

Dextro and levo compounds are not obtained by synthesis; in fact, synthetic compounds containing an asymmetric carbon atom are almost invariably optically inactive. For instance, synthetic lactic acid, obtained by the usual laboratory methods which are used for preparing alpha hydroxy propionic acid, is optically inactive. The explanation of this fact is that by synthesis we have formed at the same time an equal number of dextro and levo molecules. An inactive compound, then, contains an asymmetric carbon atom, but is optically inactive because it consists of an equal number of molecules of the dextro and levo compounds which rotate the plane of polarization an equal amount but in opposite directions. This explanation agrees with the experimental facts, for we have previously shown that inactive lactic acid can be decomposed into the dextro and levo lactic acids, which can be combined again to form inactive lactic acid, the (*d+l*) variety. The active lactic acids are therefore represented in a satisfactory manner by the solid tetrahedral formulas which show that they are the same chemically but different physically. The inactive lactic acid is represented by two tetrahedra, one of which is dextro and the other levo, and for brevity designated simply as *i*-lactic acid.

The solid formulas which are used to represent optically active compounds (stereoisomers) are called *stereochemical formulas* and are conveniently represented by plane projections which are formulas expressed in writing instead of solid figures. The written stereochemical formulas of the two active lactic acids would be as represented below :



Like the solid formulas which they represent, one of the written formulas is, of course, a mirror image of the other.

## HYDROCARBONS, HYDROXY ACIDS, AND DIBASIC ACIDS

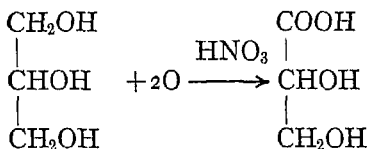
HYDRO-CARBONS	MONOHYDROXY MONOCARBOXYL ACIDS	DIHYDROXY MONOCARBOXYL ACIDS	DIBASIC ACIDS	MONOHYDROXY DICARBOXYL ACIDS	DIHYDROXY DICARBOXYL ACIDS
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \\ \text{methane} \end{array}$	$\begin{array}{c} \text{CH}_2 < \begin{array}{l} \text{OH} \\ \text{COOH} \end{array} \\ \text{glycolic} \end{array}$		$\begin{array}{c} \text{CH}_2 < \begin{array}{l} \text{COOH} \\ \text{COOH} \end{array} \\ \text{malonic} \end{array}$	$\begin{array}{c} \text{CH}(\text{OH})(\text{COOH})_2 \\ \text{tartronic} \end{array}$	
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \\ \text{ethane} \end{array}$	$\begin{array}{c} \text{CH} < \begin{array}{l} \text{OH} \\ \text{COOH} \end{array} \\   \\ \text{CH}_3 \\ \text{lactic} \\ 3 \text{ varieties} \\ d, l, \text{ and } i \end{array}$	$\begin{array}{c} \text{CH} < \begin{array}{l} \text{OH} \\ \text{COOH} \end{array} \\   \\ \text{CH}_2\text{OH} \\ \text{glyceric} \\ 3 \text{ varieties} \\ d, l, \text{ and } i \end{array}$	$\begin{array}{c} \text{CH}(\text{COOH})_2 \\   \\ \text{CH}_3 \\ \text{isosuccinic} \end{array}$		
	$\begin{array}{c} \text{CH}_2\text{OH} \\ \text{CH}_2\text{COOH} \\ \text{hydracrylic} \end{array}$		$\begin{array}{c} \text{CH}_2\text{COOH} \\ \text{CH}_2\text{COOH} \\ \text{succinic} \end{array}$	$\begin{array}{c} \text{CH}(\text{OH})(\text{COOH}) \\   \\ \text{CH}_2\text{COOH} \\ \text{malic} \\ 3 \text{ varieties} \\ d, l, \text{ and } i \end{array}$	$\begin{array}{c} \text{CH}(\text{OH})(\text{COOH}) \\   \\ \text{CH}(\text{OH})(\text{COOH}) \\ \text{tartaric} \\ 4 \text{ varieties} \\ d\text{-tartaric} \\ l\text{-tartaric} \\ i\text{-racemic} \\ i\text{-mesotartaric} \end{array}$

In addition to the simple hydroxy acids which we have already studied, there are a number of other hydroxy acids, some of which are well-known substances. In the table above are included

the simple hydroxy acids we have already considered and in addition a few of the more complex hydroxy acids. There are also included the dibasic acids which are closely related to these compounds and the hydrocarbons from which these various substances are derived. The carbon atoms which are inclosed in circles are asymmetric carbon atoms.

Glyceric acid,  $\begin{array}{c} \text{CHOHCOOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ , is the monohydroxy derivative

of lactic acid, or the dihydroxy derivative of propionic acid. It contains an asymmetric carbon atom, and like the lactic acids, there are three varieties: dextro, levo, and inactive. These three varieties of glyceric acid have the same general chemical behavior and therefore the same structural formula. They differ only in their behavior toward polarized light, and in accordance with the theory of stereochemistry are distinguished by their stereochemical formulas. The inactive glyceric acid may be prepared by the careful oxidation of glycerol with nitric acid:



It is a thick liquid which is soluble in water and alcohol, but insoluble in ether. It may be decomposed into the optically active dextro and levo glyceric acids.

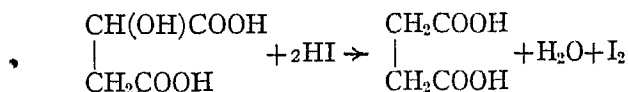
**Tartronic acid**  $\text{CH}(\text{OH})(\text{COOH})_2$ , is the monohydroxy derivative of malonic acid,  $\text{CH}_2(\text{COOH})_2$ . It may be prepared from malonic acid by the usual methods of substituting hydrogen by the hydroxyl group. By the interaction of malonic acid and bromine, monobrom malonic acid,  $\text{CHBr}(\text{COOH})_2$ , is obtained, and this substance when treated with silver hydroxide yields tartronic acid:



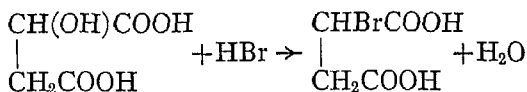
Tartronic acid is obtained from its aqueous solution as crystals which melt at  $187^{\circ}$ .

Malic acid,  $\begin{array}{c} \text{CH(OH)COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ , is the monohydroxy derivative of succinic acid,  $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CH}_2\text{COOH} \end{array}$ . Malic acid contains an asymmetric

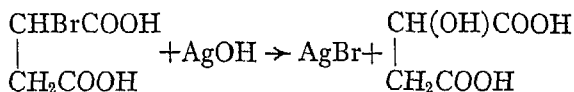
carbon atom, and there are three varieties: dextro, levo, and inactive. The well-known, or common, variety of malic acid is obtained from unripe apples and occurs very generally in the juices of fruits such as gooseberries, currants, and strawberries. The sourness of unripe fruit is generally due to the presence of tartaric, citric, and malic acids, which are sometimes called *vegetable acids*. Malic acid is readily prepared from the berries of the unripe mountain ash. The juice of the berries is neutralized with calcium hydroxide. When this solution is evaporated, the calcium salt of malic acid is obtained. Malic acid is obtained from a solution of the calcium salt by adding the required amount of sulfuric acid, filtering off the insoluble calcium sulfate, and evaporating the filtrate. A dilute solution of malic acid obtained from fruit juices is levo rotatory. The solution, however, shows an unusual behavior. When the solution is gradually concentrated, the levo rotation is decreased until it becomes zero. On further concentration the solution becomes dextro rotatory. Malic acid is a crystalline substance which melts at  $100^{\circ}$  and is very soluble in alcohol and water. Its structure represents its chemical behavior. When reduced with hydrogen iodide it yields succinic acid:



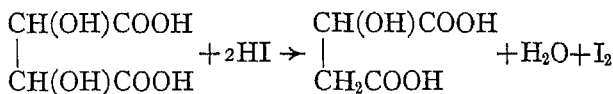
It interacts with hydrogen bromide, forming monobrom succinic acid:



**Inactive and dextro malic acids.** Brom succinic acid may be obtained as shown above from malic acid or by the interaction of succinic acid and bromine. When brom succinic acid is treated with silver hydroxide, inactive malic acid is obtained :

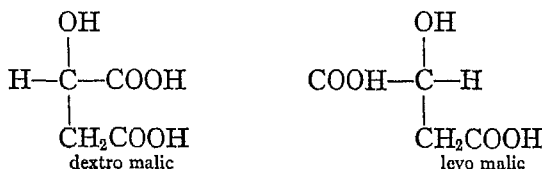


It is obtained also by the hydrogen iodide reduction of racemic acid, which is an inactive variety of the tartaric acids :



It may also be prepared by mixing solutions containing equal parts of dextro and levo malic acids. Inactive malic acid crystallizes easily from its aqueous solutions and is readily soluble in water and alcohol. It melts at  $130^\circ$ .

Just as the dextro and levo lactic acids may be obtained from inactive lactic acid by fractional crystallization, in a similar manner inactive malic acid may be split up into the dextro and levo varieties. When the cinchonine salt of inactive malic acid is allowed to crystallize, the cinchonine salts of dextro and ordinary levo malic acids are obtained. Dextro and levo malic acids may be obtained from their cinchonine salts. Their written stereochemical formulas would be as represented below :





Like inactive lactic acid, the inactive malic acid consists of an equal number of molecules of the dextro and levo malic acids. Dextro malic acid may also be obtained by the hydrogen iodide reduction of dextro tartaric acid. It melts at  $100^{\circ}$ .

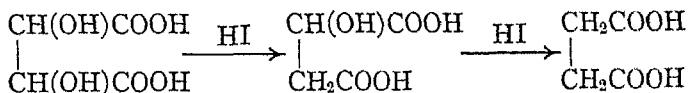
**Tartaric acid.** There are four tartaric acids having the formula  $\begin{array}{c} \text{CH(OH)COOH} \\ | \\ \text{CH(OH)COOH} \end{array}$ . They are called *dextro tartaric*, *levo tartaric*, *inactive racemic*, and *inactive mesotartaric*. These tartaric acids are dihydroxy derivatives of succinic acid and contain two asymmetric carbon atoms.

Dextro tartaric acid (commonly called *tartaric acid*) is the well-known, or common, variety of the tartaric acids. It occurs in many different kinds of fruits as the acid itself or in the form of its potassium or calcium salts. The acid potassium salt of

tartaric acid,  $\begin{array}{c} \text{CH(OH)COOH} \\ | \\ \text{CH(OH)COOK} \end{array}$ , commonly called *cream of tartar*,

is also a constituent of various kinds of fruits and occurs in considerable quantity in the juice of grapes, from which the acid is obtained commercially. When grape juice is allowed to ferment in preparing wine, the acid potassium tartrate, being difficultly soluble, is precipitated together with tannin and other impurities as crystalline crusts known as *argol*. The acid salt is obtained from the impure argol by crystallization. By treating the acid salt with chalk (calcium carbonate), insoluble calcium tartrate is obtained. Tartaric acid is prepared from the calcium salt by treating with sulfuric acid.

The reactions of tartaric acid show that it is a dihydroxy derivative of succinic acid. When treated with hydrogen iodide it is reduced to dextro malic acid, which on further reduction is converted into succinic acid:

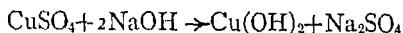


Tartaric acid crystallizes in transparent monoclinic prisms which are soluble in water and alcohol and melt at  $168^{\circ}$  to  $170^{\circ}$ . When heated above its melting point, it is decomposed. The acid and its salts are used extensively in certain commercial and medicinal applications. Tartaric acid in solution is easily oxidized. An ammoniacal solution of silver nitrate is reduced by it, forming a silver mirror. Tartaric acid prevents the precipitation of the hydroxides of certain metals from their salt solutions. Copper hydroxide, for instance, is not precipitated from copper sulfate by sodium hydroxide if tartaric acid is present.

#### EXPERIMENT 49

##### Tartaric acid and tartrates

**A. Reaction of alkaline tartrate solution.** Add a solution of sodium hydroxide (1 : 10) to about 3 cc. of a solution of copper sulfate (1 : 10). Copper hydroxide is precipitated:



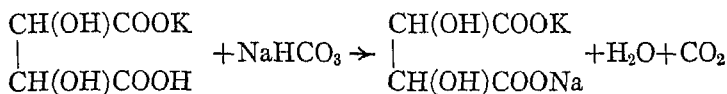
Add 3 cc. of a solution of tartaric acid (1 : 10) to about 3 cc. of a solution of copper sulfate (1 : 10). Now make the mixture alkaline with sodium hydroxide solution (1 : 10). The tartaric acid prevents the precipitation of the copper as hydroxide by forming with it a complex soluble compound.

**B. Silver mirror test.** Add slowly a silver nitrate solution (1 : 10) to about 4 cc. of a solution of tartaric acid (1 : 10). Silver tartrate is precipitated. Now add a few drops of dilute ammonia (1 : 10) until the precipitate is nearly dissolved. When the test tube is placed in a beaker of water heated to about  $60^{\circ}$ , a silver mirror is deposited.

**Cream of tartar** (potassium hydrogen tartrate),  $\begin{matrix} \text{CHOHCOOH} \\ | \\ \text{CHOHCOOK} \end{matrix}$ ,

is used as an ingredient in tartrate baking powders. In making bread, which consists essentially of flour with the addition of a little salt and water, the dough which is at first obtained is heavy and thick. This is rendered light by various methods, one of which is the use of baking powders. Tartrate baking powders

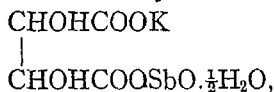
consist of sodium bicarbonate, potassium bitartrate, and starch which serves as a diluent for the bicarbonate and bitartrate. When water is added to baking powder, the bitartrate and bicarbonate react and carbon dioxide is evolved. As the carbon dioxide escapes it renders the dough light:



**Rochelle salt** (sodium potassium tartrate),  $\begin{array}{c} \text{CHOHCOONa} \\ | \\ \text{CHOHCOOK} \end{array}$ , is

used considerably in medicine as a purgative. Seidlitz powders consist of a mixture of rochelle salt and sodium bicarbonate in one powder and tartaric acid in another. When solutions of the two powders are mixed, carbon dioxide is evolved. Rochelle salt is also used in preparing Fehling's solution, which is an alkaline tartrate solution. Fehling's solution is a mild oxidizing agent and is used in testing the reducing power of carbohydrates (see Fehling's solution, page 248).

**Tartar emetic** (potassium antimonyl tartrate),

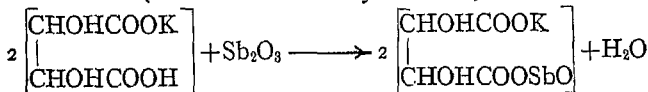


is a substance which has an irritating effect on the alimentary canal and causes vomiting. It is used as an emetic. It is readily soluble in water and is also used as a mordant. Tartar emetic is prepared by the interaction of potassium hydrogen tartrate and antimony trioxide.

#### EXPERIMENT 50

**Preparation of tartar emetic,**  $\begin{array}{c} \text{CH(OH)COOK} \\ | \\ \text{CH(OH)COOSbO} \cdot \frac{1}{2}\text{H}_2\text{O} \end{array}$

(Potassium antimonyl tartrate)



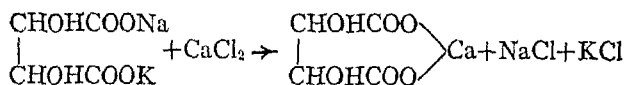
*Materials*  $\left\{ \begin{array}{l} 5 \text{ grams of potassium hydrogen tartrate} \\ 6 \text{ grams of antimony trioxide} \end{array} \right.$

*Procedure.* Dissolve 5 grams of potassium hydrogen tartrate in about 60 cc. of water. Add 6 grams of antimony trioxide. The mixture is boiled about 10 minutes, filtered, and the filtrate allowed to crystallize. The crystals are filtered off and dried on filter paper. Preserve a specimen.

Calcium tartrate,  $\begin{array}{c} \text{CHOHCOO} \\ | \\ \text{CHOHCOO} \end{array} \text{Ca}$ , is precipitated when a solution of a calcium salt is added to a neutral solution of a tartrate.

#### EXPERIMENT 51

Preparation of calcium tartrate,  $\begin{array}{c} \text{CHOHCOO} \\ | \\ \text{CHOHCOO} \end{array} \text{Ca}$

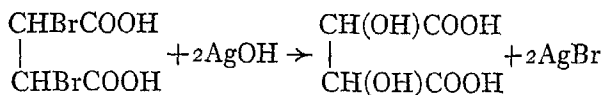


*Materials*  $\left\{ \begin{array}{l} 2 \text{ grams of sodium potassium tartrate} \\ \text{Calcium chloride solution (1 : 10)} \end{array} \right.$

*Procedure.* Dissolve 2 grams of sodium potassium tartrate in about 20 cc. of water. Add a calcium chloride solution (1 : 10) until the white calcium tartrate is completely precipitated. Filter, and wash the precipitate. Dry on filter paper, and preserve a specimen. Try the solubility of this salt in potassium hydroxide solution.

**Racemic acid** is the inactive, or (*d+l*), variety of the tartaric acids, corresponding to the inactive form of lactic and malic acids. It occurs naturally with tartaric acid and tartrates in fruit juices either as the acid itself or in the form of its salts. Racemic acid is formed to some extent when tartaric acid is boiled with a solution of sodium hydroxide or hydrogen chloride. When tartaric acid is boiled with an excess of sodium hydroxide, it is gradually converted into sodium racemate, which is converted into racemic acid by precipitating it as calcium racemate

and decomposing the calcium salt with sulfuric acid. It may be prepared synthetically together with mesotartaric acid by the interaction of dibrom succinic acid and silver hydroxide:



Although racemic acid has the same composition as tartaric acid, it differs from it in several respects. It melts at  $205^{\circ}$ – $206^{\circ}$ . It is not quite as soluble as tartaric acid, and a solution of it is optically inactive.

**Separation of racemic acid into the optically active tartaric acids.** Racemic acid is interesting historically, as it was the first inactive compound to be decomposed into optically active isomers. In 1848 Pasteur discovered that if a solution of sodium

ammonium racemate,  $\begin{array}{c} \text{CHOHCOONa} \\ | \\ \text{CHOHCOONH}_4 \cdot 4\text{H}_2\text{O} \end{array}$ , is allowed to

evaporate, two sets of crystals are obtained. Crystals of one set, containing dextro-hemihedral faces, were found to be the mirror image of the crystals of the other set, which contained levo-hemihedral faces. These two kinds of crystals were separated mechanically and dissolved in water. The solution which contained the crystals having right-handed faces showed a dextro rotation, while the solution containing the crystals having left-handed faces was found to be levo rotatory. When the dextro and levo crystals were decomposed and converted into the corresponding tartaric acids, one of the acids obtained was found to be ordinary dextro tartaric acid, while the other was the isomeric levo tartaric acid.

Pasteur not only decomposed racemic acid into dextro and levo tartaric acids, but he prepared racemic acid synthetically by mixing solutions containing equal weights of dextro and levo tartaric acids and allowing the mixture to crystallize. Pasteur also devised other methods of separating a racemic form of an

optically active substance into its optically active isomers. He showed that by combining the active tartaric acids with an organic base such as cinchonine, the resulting salts had different solubilities, and consequently by preparing the cinchonine salt of racemic acid and allowing it to crystallize, the cinchonine salts of dextro and levo tartaric acids could be obtained.

Another method of separating a racemic modification into its optically active constituents consists in treating the mixture with certain organisms which destroy one active modification, leaving the other. Thus when the mold, *Penicillium glaucum*, is allowed to grow in a solution of ammonium racemate, it destroys the ammonium salt of dextro tartaric acid by using it as food and leaves the ammonium salt of levo tartaric acid.

The inactivity of racemic acid, which consists of an equal number of molecules of dextro and levo tartaric acids, is due to external compensation. The dextro rotation of the dextro acid is neutralized by the levo rotation of the levo acid. Since racemic acid and the tartaric acids were the first optically active substances to be investigated, the term "racemic" is often used as a general expression to designate an inactive substance which may be decomposed into its optically active constituents.

**Levo tartaric acid** may be prepared from racemic acid by the general methods we have just described. It melts at  $170^{\circ}$  and resembles ordinary dextro tartaric in its general chemical behavior, except in its action on polarized light. It rotates the plane of polarization to the left, while dextro tartaric rotates to the right. The number of degrees of rotation is the same in each case. The sodium ammonium salts of the dextro and levo acids, as we have previously explained, crystallize in forms which are the mirror images of each other.

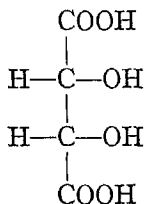
**Mesotartaric acid** is obtained together with racemic acid when dextro tartaric is heated with water at  $165^{\circ}$  for about 2 days. It is also formed along with racemic acid by the interaction of dibrom succinic acid and silver hydroxide. Mesotartaric acid

is rather more soluble than racemic acid. The acid potassium salt of mesotartaric acid is also more soluble than the acid potassium salt of dextro or levo tartaric acids. Mesotartaric acid crystallizes with one molecule of water of crystallization, and the anhydrous acid melts at  $140^{\circ}$ . Its solutions are optically inactive and it cannot be decomposed into optically active isomers.

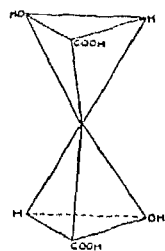
**Stereochemistry of the tartaric acids.** As we have previously explained, there are four dihydroxy succinic acids having the

structural formula  $\begin{array}{c} \text{CH(OH)COOH} \\ | \\ \text{CH(OH)COOH} \end{array}$ . Each of these substances

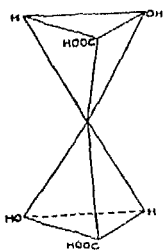
is crystalline and contains two asymmetric carbon atoms. Dextro and levo tartaric acids are optically active and have the same degree of rotation but in opposite directions. Their crystal forms are different, their cinchonine salts have different solubilities, and they behave differently toward certain organisms. Racemic and mesotartaric acids are both inactive, but racemic acid, unlike mesotartaric, may be resolved into the optically active dextro and levo tartaric acids. Racemic and mesotartaric acids also differ from each other and from the active tartaric acids in their melting points, crystalline form, and the solubility of certain of their salts. Since the tartaric acids contain two asymmetric carbon atoms, the stereochemistry of these compounds is somewhat more complex than that of the lactic or malic acids. The structural formulas of the tartaric acids show that each of the asymmetric carbon atoms is joined to an atom of hydrogen, the hydroxyl and carboxyl groups, and the  $\text{CH(OH)COOH}$  group as represented below:



If we endeavor to represent this structure as a solid figure in three dimensions of space, then according to the stereochemical theory of Van't Hoff and Le Bel this structure must be represented by two tetrahedra connected together at a solid angle of each and having an asymmetric carbon atom at the center of each tetrahedron. The groups which are situated at the



Dextro tartaric



Levo tartaric



Figure 20

other solid angles of this double tetrahedron may be arranged around the asymmetric carbon atoms in two different ways. One arrangement, representing dextro tartaric acid, is the mirror image of the other, representing levo tartaric acid. The solid formulas of dextro and levo tartaric acids are given in Figure 20, and under them are the plane projections or written stereochemical formulas of these acids.

As shown by the solid formula of dextro tartaric acid, the special relations of the groups around the central carbon atoms are identical. By casually inspecting the figure this may not appear to be true, but by dividing the double tetrahedron into two single ones at their common point of contact, turning the top one over, and placing it alongside the lower one, it will be seen that the arrangement of the groups around the central carbon atom is the same in each tetrahedron. The diagrams shown in Figure 21 represent the double tetrahedron of dextro tartaric acid divided into two single ones which are identical.

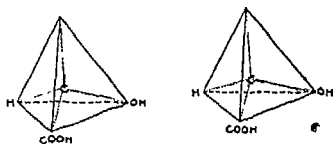


Figure 21

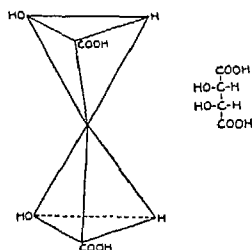
As explained by the diagrams above, in the double tetrahedron, or solid formula, of dextro tartaric acid the spatial relations of



the groups around the central asymmetric carbon atoms are identical. We thus have a positive arrangement in the upper tetrahedron over a positive arrangement in the lower one, and the optical rotation is therefore intensified and we have a dextro compound.

The same idea obtains for levo tartaric acid, where the spatial arrangement of the groups around the central carbon atoms is identical but opposite to that in dextro tartaric acid.

Mesotartaric acid may also be represented by a double tetrahedron, as shown in Figure 22. In mesotartaric acid the arrangement of the groups around the central carbon atom in the upper tetrahedron is the opposite of that in the lower one. This may be shown by cutting the double tetrahedron in half and placing the two single tetrahedrons side by side.



Mesotartaric acid

Figure 22

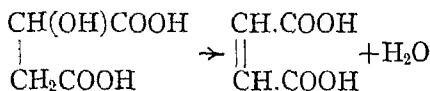
We have, then, in mesotartaric acid a positive arrangement above a negative one, and therefore the rotatory power of one part of the molecule is neutralized by that of the other part and optical inactivity is due to internal compensation.

Racemic acid is simply a mixture of an equal number of molecules of dextro and levo tartaric acids. This is proved by the fact that racemic acid may be decomposed into dextro and levo tartaric acids, which may be combined again to form racemic acid. In racemic acid, then, the dextro rotation of the dextro molecules is neutralized by the levo rotation of the levo molecules, and the compound is inactive due to external compensation.

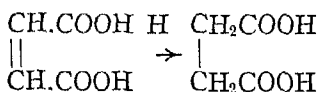
**Maleic and fumaric acids.** There are two other acids closely related to malic acid which are interesting from a stereochemical standpoint and therefore may now be conveniently considered. They are the isomeric unsaturated dibasic acids, maleic and

fumaric, having the formula  $\begin{array}{c} \text{CH.COOH} \\ || \\ \text{CH.COOH} \end{array}$ . As shown by the

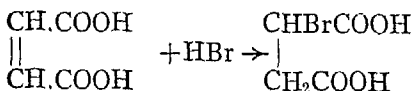
formula, they are dicarboxyl derivatives of ethylene. Their structure is determined by their methods of preparation and chemical behavior. Both acids may be prepared by distilling the common variety of malic acid obtained from fruits. Maleïc acid and its anhydride are distilled over, while fumaric acid remains behind in the flask :



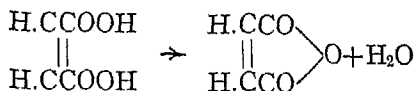
Both of these acids are reduced to succinic acid by nascent hydrogen or hydrogen iodide,



and react with hydrogen bromide, yielding brom succinic acid,



Maleïc acid,  $\begin{array}{c} \text{HCCOOH} \\ || \\ \text{HCCOOH} \end{array}$ , is a crystalline substance having an acid taste. It melts at  $130^\circ$  and boils at  $160^\circ$ , decomposing partially into water and its anhydride,



The anhydride is a crystalline substance melting at  $60^\circ$  and reacts readily with water, forming maleïc acid. When maleïc acid is heated with water at  $130^\circ$ , it is converted into fumaric acid.

$$\begin{array}{c} \text{H CCOOH} \\ || \\ \text{COOHC.H} \end{array}$$
 Fumaric acid, , occurs naturally in certain

plants such as the fungi. It has an acid taste and is difficultly soluble in cold water. When heated it does not melt but sublimes at 200°, and at higher temperature is decomposed into maleïc anhydride and water. Since maleïc anhydride is easily converted into maleïc acid by water, this reaction furnishes a means of converting one isomer into the other.

Maleïc and fumaric acids contain no asymmetric carbon atoms and are not optically active. Although these acids have different solubilities and behave differently when heated, they both have the same structure, as shown by their reactions with hydrogen bromide, which yields brom succinic acid, and by reduction with hydrogen, which converts them into succinic acid. The structure of maleïc and fumaric acids and the relations between these compounds may be explained in accordance with the theory of stereochemistry, which requires in this case a somewhat further extension. We have already shown that compounds such as the lactic and malic acids which contain one asymmetric carbon atom may be represented by a tetrahedron, or solid formula. Compounds such as the tartaric acids, which contain two asymmetric carbon atoms, may be represented by two tetrahedra joined together at one of their solid angles. The unsaturated condition of compounds containing a double bond such as maleïc and fumaric acids may be represented stereochemically by two tetrahedra united by a common edge. If, as in the case of maleïc and fumaric acids, each of the double-bond carbon atoms is united to different atoms or groups, then there are two ways in which the structure of these compounds can be arranged in space, as shown by the solid figures in Figure 23, under which are the written stereochemical formulas. Both compounds are represented by a double tetrahedron joined together by a common edge. Maleïc acid is represented by a solid formula



in which both carboxyl groups are on the same side (cis formula). The reason for this is that when maleic acid is heated it yields maleic anhydride. Since the anhydride is obtained by the interaction of two carboxyl groups, it is evident that if the carboxyl groups are near each other they can react more readily with the elimination of water. When fumaric acid is heated it

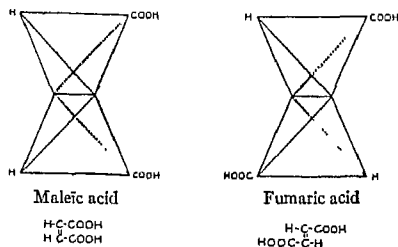


Figure 23

does not decompose, yielding fumaric anhydride, and this fact is represented by the solid formula in which the two carboxyl groups are on opposite sides (trans formula), showing that it is not easy for them to come together and react chemically. This further development of the theory of stereochemistry applies to a number of other cases of isomeric compounds, such as the maleic and fumaric acids, and is considered a satisfactory explanation for the behavior of such substances.

The outline equations on the opposite page show how many of the various hydroxy acids which we have considered may be obtained from ethyl alcohol by a series of reactions.

## QUESTIONS

1. What are hydroxy acids?
2. Write equations showing the preparation of glycolic acid from ethylene glycol, chloroacetic acid, or aminoacetic acid.
3. Write the structural formulas of alpha and beta hydroxy propionic acids.
4. Show by outline equations how alpha and beta hydroxy propionic acids may be obtained from ethyl alcohol.
5. What products are obtained by distilling inactive lactic acid with sulfuric acid? How are these products tested?
6. How do the three isomeric lactic acids act toward polarized light?
7. What is meant by "plane polarized light," "rotation of the plane of polarization," and "optically active substances"?
8. Explain the essential features of a polariscope. How is the rotation of the plane of polarization determined?
9. Upon what factors does the rotation of the plane of polarization depend?
10. What formulas are used to determine the specific and molecular rotation?
11. What is meant by the terms "dextro," "levo," and "inactive"?
12. How is inactive lactic acid separated into dextro and levo lactic acids?
13. What is meant by stereochemistry?
14. What is an asymmetric carbon atom?
15. Draw the solid stereochemical formulas of dextro and levo lactic acids. Is one of these formulas the mirror image of the other?
16. Why is it that synthetic compounds containing an asymmetric carbon atom are optically inactive?
17. Show how the active lactic acids are represented by written stereochemical formulas.
18. From what hydrocarbons are lactic, glyceric, malic, and tartaric acids derived?
19. Write the complete structural formulas of malic and tartaric acids.
20. Draw the stereochemical formulas of dextro and levo malic acids.
21. How does dextro tartaric acid occur? How is it tested?
22. For what purposes are the following compounds used: cream of tartar; Rochelle salt; tartar emetic?
23. Explain, with equations, the preparation of tartar emetic and calcium tartrate.
24. Show how dextro, levo, and mesotartaric acids are represented by solid and written stereochemical formulas.
25. Explain the inactivity of racemic and mesotartaric acids.
26. Show how maleic and fumaric acids are represented by solid and written stereochemical formulas.

## CHAPTER SIXTEEN

### CARBOHYDRATES

THE carbohydrates form one of the most important groups of organic compounds. Many of these substances occur naturally in growing plants. This group includes many well-known and important compounds such as the sugars, starches, and cellulose. The sugars are valuable as foods and as a source of alcohol, and they give to fruits their sweet taste. The starches serve as a valuable and abundant source of food, and the celluloses are substances which compose to a great extent the cell walls and tissues of plants. In view of these facts it is evident that the carbohydrates are compounds of unusual importance and interest.

The term "carbohydrate" was applied originally to those substances, such as cane sugar,  $C_{12}H_{22}O_{11}$ , which occur naturally in plants and contain also, in addition to carbon, hydrogen and oxygen in the same proportion as they are present in water. In view of their composition and the fact that when heated out of contact with the air water is given off and a deposit of carbon remains, it was formerly believed that these substances consist of carbon and water. They do not, however, contain water and, therefore, are not hydrates of carbon, as the name implies.

The carbohydrates are usually divided into three general classes :

I. **Monosaccharides**, or monoses, are simple sugars, many of which have the formula  $C_6H_{12}O_6$ . As examples of this class we have the compounds glucose and fructose.

II. **Polysaccharides which are sugars** are more complex in structure than the monosaccharides, or simple sugars. Many of them, such as cane sugar and milk sugar, have the formula  $C_{12}H_{22}O_{11}$  and are sometimes called *disaccharides*. Others, such as raffinose,  $C_{18}H_{32}O_{16} \cdot 5H_2O$ , which is a trisaccharide, are still more complex in structure.

III. Polysaccharides which are not sugars are very complex substances which have the formula  $(C_6H_{10}O_5)_n$ . As examples of this class we have starch, dextrin, and cellulose.

We have, then, three classes of carbohydrates — monosaccharides, polysaccharides which are sugars, and polysaccharides which are not sugars.

#### EXPERIMENT 52

##### Carbohydrate color test

(Molisch's reaction)

Add 2 drops of a 10 per cent solution of alpha naphthol dissolved in chloroform to a very small quantity (0.1 gram) of cane sugar in a test tube. Hold the tube in an inclined position and pour carefully 2 cc. of concentrated sulfuric acid down the side of the test tube, so that the contents of the test tube will be divided into two layers and not mixed. Allow the tube to stand a few seconds. The formation of a purple-red ring indicates the presence of a carbohydrate.

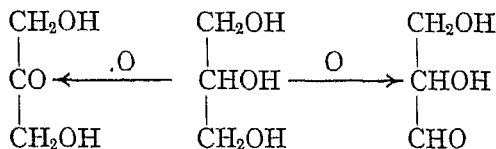
The monosaccharides (monoses), which are the simplest carbohydrates, are not hydrolyzed into simpler substances. There are two kinds of monosaccharides. Those containing aldehyde and alcohol groups, such as aldehyde-alcohols, are known as *aldoses*. Those which are ketone-alcohols, such as fructose, are called *ketoses*. The monosaccharides are distinguished further in accordance with the number of carbon atoms they contain. Those containing three carbon atoms (glycerose,  $C_3H_6O_3$ ) are *trioses*. *Tetroses* (erythrose,  $C_4H_8O_4$ ) contain four carbon atoms. *Pentoses* contain five carbon atoms; and sugars which have a larger number of carbon atoms, such as the *hexoses*, *heptoses*, *octoses*, and *nonoses*, are also known.

The monosaccharides are soluble in water and give solutions which have a sweet taste. They crystallize from their solutions as colorless crystals. When heated above the melting point, they decompose and become brown in color. Most of them contain asymmetric carbon atoms and, excepting the racemic varieties, are optically active.

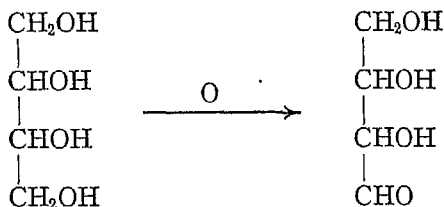


**Carbohydrates containing less than six carbon atoms.** There are a number of carbohydrates containing less than six carbon atoms. Only a few of these are especially important. The

simplest aldose is glycolic aldehyde,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHO} \end{array}$ , which is obtained by the oxidation of ethylene glycol,  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ . Glycerose, a mixture of trioses, is obtained by the oxidation of glycerol:



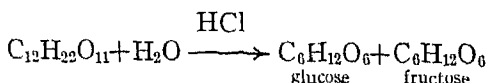
It consists of a mixture of glyceric aldehyde,  $\text{CH}(\text{OH}) < \begin{array}{c} \text{CH}_2\text{OH} \\ \text{CHO} \end{array}$ , which is one of the simplest aldoses, and dihydroxy acetone,  $\text{CO} < \begin{array}{c} \text{CH}_2\text{OH} \\ \text{CH}_2\text{OH} \end{array}$ , the simplest ketose. Glycerose is a sweet syrup and reduces Fehling's solution. It therefore behaves like many of the other sugars. Erythrose,  $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{CHO}$ , is a tetrose obtained by the oxidation of erythritol,  $\text{CH}_2\text{OH}(\text{CHOH})_2\text{CH}_2\text{OH}$ :



Arabinose and xylose are stereoisomeric pentoses having the formula  $\text{CH}_2\text{OH}(\text{CHOH})_3\text{CHO}$ . They have a sweet taste, reduce Fehling's solution, but do not ferment with yeast. Arabinose is obtained from gum arabic or cherry gum by boiling

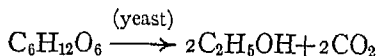
with dilute sulfuric acid. Xylose, or wood sugar, is prepared from wood gum by boiling beech wood, jute, straw, and certain other vegetable products with dilute acids. These natural gums contain complex substances known as *pentosans*, which occur naturally in the cellular parts of many plants. The pentosans yield pentose sugars when hydrolyzed and are useful as animal foods. In the analysis of foods such as farm crops for domestic animals the pentosans are regarded as an important constituent to be determined. The method of analysis consists in hydrolyzing the pentosans with a hot acid solution. The pentoses which are obtained first are further hydrolyzed into furfural,  $C_4H_3O.CHO$ , an aldehyde derivative of furfuran, yields when treated with phloroglucinol,  $C_6H_3(OH)_3$ , an insoluble compound which may be weighed accurately, and from this weight the amount of pentosans and pentoses may be calculated.

**Hexoses.** The hexoses are the most important of the monosaccharides. Glucose and fructose, having the molecular formula  $C_6H_{12}O_6$ , are the most important of the hexoses. These two simple sugars are widely distributed in the vegetable kingdom. They occur naturally in the juices of many different kinds of sweet fruits, in flowers, and in honey. They may be prepared from cane sugar,  $C_{12}H_{22}O_{11}$ . When cane sugar is hydrolyzed in the presence of dilute acids, glucose and fructose are obtained in equal amounts and the mixture is known as invert sugar:

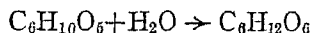


These two isomeric sugars are optically active, the glucose being dextro rotatory, while fructose has a levo rotation. Since the negative rotation of fructose is greater than the positive rotation of glucose, invert sugar, which contains equal amounts of both sugars, is levo rotatory. As cane sugar itself is dextro rotatory, while invert sugar has the opposite rotation, the pro-

cess of decomposing cane sugar by hydrolysis is known as *inversion*. Both glucose and fructose are fermented by yeast, yielding principally alcohol and carbon dioxide :



**Glucose**,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO}$ , occurs naturally in grapes and hence is sometimes called *grape sugar*. As it is dextro rotatory, it is also known as *dextrose*. When grapes are dried in the sun in preparing raisins, the glucose in the juice is deposited in brown-colored crusts. Glucose occurs also in the urine in cases of diabetes. It may be obtained by hydrolyzing various polysaccharides such as starch, cellulose, and dextrin in the presence of dilute acids :



Since glucose is further hydrolyzed into alcohol, it is thus possible to convert wood and other fibers which contain cellulose into glucose and alcohol. In a similar manner corn, potatoes, and other substances containing starch may be hydrolyzed into glucose and alcohol. Glucose is manufactured commercially from corn, potatoes, rice, and other substances containing starch. When corn starch is used as a source of glucose, the material is boiled with a dilute solution of hydrogen chloride. If commercial glucose syrup is desired, the boiling is continued until a portion of the solution tested for starch with iodine no longer gives a blue color. This impure syrup thus obtained contains also, in addition to glucose, some dextrin and maltose. If it is desired to convert the starch completely into glucose, the boiling is continued somewhat longer until a portion tested with alcohol gives no precipitate, thus showing the absence of starch and dextrin, which are insoluble in alcohol. The dilute solution thus obtained is neutralized with sodium carbonate, decolorized with bone black, and evaporated in vacuum pans until it crystallizes on cooling. Glucose is obtained as a compact crystalline mass.

Glucose is used to strengthen wines and beers by adding it to such solutions before fermentation. It is used as a table syrup and in the manufacture of confectionery, jellies, and such products. It crystallizes from dilute aqueous solutions with one molecule of water of crystallization. When crystallized from 95 per cent alcohol, anhydrous glucose melting at  $146^{\circ}$  is obtained. Pure glucose is about three fifths as sweet as cane sugar. It is quite unlike cane sugar in that it is soluble in alcohol, and is not charred by sulfuric acid. It is a strong reducing agent and quickly precipitates copper, gold, and other metals from warm solutions of their salts. It reduces an ammoniacal silver nitrate solution, forming a silver mirror, and also reduces an alkaline copper tartrate solution (Fehling's solution).

#### EXPERIMENT 53

##### Reduction of Fehling's solution by glucose

*Procedure.* (Fehling's solution may be obtained from the stock room.) Dissolve in a test tube about 0.2 gram of glucose,  $C_6H_{12}O_6$ , in 5 cc. of water; add about 4 cc. of Fehling's solution (2 cc. of alkaline tartrate solution and 2 cc. of copper sulfate solution), and boil. Red cuprous oxide is precipitated.

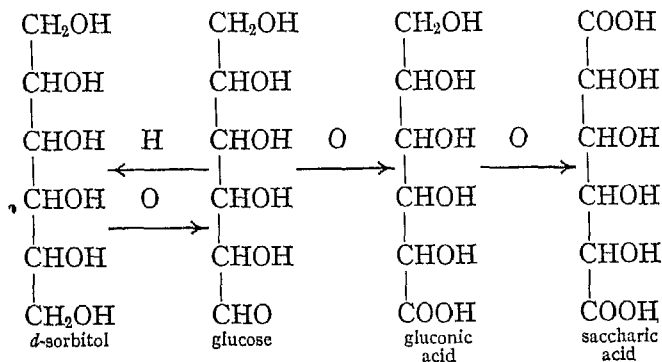
*NOTE.* Fehling's solution is prepared by mixing an alkaline tartrate solution with an equal volume of copper sulfate solution. The copper sulfate solution is prepared by dissolving 34.64 grams of copper sulfate in 500 cc. of water. The tartrate solution is made by dissolving 173 grams of sodium potassium tartrate (Rochelle salt) and 50 grams of sodium hydroxide in 500 cc. of water. Fehling's solution decomposes on standing, and hence the two solutions should be mixed just before using. It is an oxidizing solution and is made alkaline with sodium hydroxide in preparing it, because sugars are more easily oxidized in alkaline solution. Since copper is precipitated as the hydroxide with an alkali, the Rochelle salt is added to prevent this precipitation and keep the copper in solution. When Fehling's solution is reduced by carbohydrates, the oxidizing agent, copper sulfate, is reduced to the red cuprous oxide,  $Cu_2O$ .

A given quantity of glucose reduces a definite quantity of copper sulfate to cuprous oxide. One molecule of glucose reduces approximately five molecules of copper sulfate. The quantitative reduction of Fehling's solution by glucose enables us to determine the exact amount of glucose in a solution such

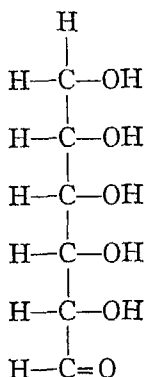
as urine and, therefore, is helpful in diagnosing cases of suspected diabetes.

Glucose combines with certain metallic salts and oxides, forming addition products such as  $C_6H_{12}O_6 \cdot NaCl$  and  $C_6H_{12}O_6 \cdot CaO$ .

**Structure.** The structure of glucose is determined in accordance with the following facts: When treated with acetic anhydride in the presence of a small amount of zinc chloride, a pentacetyl derivative of glucose is obtained, showing that glucose contains five hydroxyl groups. Since experience has shown that two hydroxyl groups united to one carbon atom give an unstable structure, it would seem probable that each hydroxyl group is united to a different carbon atom, and consequently the carbon atoms in glucose are united in a straight chain. This conclusion is verified by the fact that when glucose is reduced with sodium amalgam in aqueous solution, it is converted to *d*-sorbitol,  $CH_2OH(CHOH)_4CH_2OH$ , which is a hexahydroxyl alcohol having the carbon atoms united in a straight chain. When *d*-sorbitol is oxidized carefully, it is converted into glucose, which on further oxidation is converted into gluconic acid,  $CH_2OH(CHOH)_4COOH$ . Since gluconic acid contains the same number of carbon atoms as glucose, this reaction indicates that glucose contains an aldehyde group. When gluconic acid is oxidized, it is converted into saccharic acid,  $COOH(CHOH)_4COOH$ . These changes are indicated in the following outline equations:



Glucose is therefore an aldose containing the aldehyde group (CHO) and has the structural formula,



The table on the opposite page contains some of the monosaccharides we have considered and the alcohols which are closely related to them. There are also included the hydrocarbons from which these compounds are derived.

Fructose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , occurs in many different kinds of fruits and is known as *fruit sugar*. Since it is levo rotatory, it is also called *levulose*. The monosaccharides are not named in accordance with their optical rotation. Although fructose has a levo rotation, it is designated as *d-fructose* because it can be obtained from *d*-glucose and is closely related to other dextro substances. Fructose may be obtained by hydrolyzing various polysaccharides. When cane sugar is hydrolyzed with dilute sulfuric acid, invert sugar is obtained which consists of a mixture of glucose and fructose. The excess of acid is removed by adding powdered calcium carbonate. The insoluble calcium sulfate is filtered off, and the filtrate cooled with ice and treated with calcium hydroxide. The insoluble lime compound of fructose is precipitated, filtered off, washed, and placed in water. The lime compound is now decomposed with carbon dioxide, the insoluble calcium carbonate filtered off, and the filtrate evaporated to a syrup. Fructose is obtained from the syrup as

## HYDROCARBONS, ALCOHOLS, AND MONOSACCHARIDES

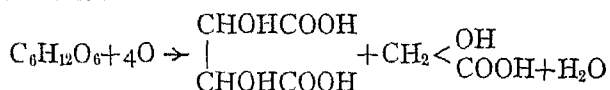
Hydrocarbons	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \\ \text{ethane} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \\ \text{propane} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \\ \text{normal butane} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \\ \text{normal pentane} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \\ \text{normal hexane} \end{array}$
Alcohols	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \\ \text{ethylene glycol} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OH} \\ \text{glycerol} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OH} \\ \text{erythritol} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OH} \\ \text{arabitol} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CH}_2\text{OH} \\ \text{d-sorbitol} \end{array}$
Monosaccharides (simple sugars)	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHO} \\ \text{glycolic aldehyde} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CHO} \\ \text{glyceric aldehyde} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHO} \\ \text{erythrose} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHO} \\ \text{arabinose} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHOH} \\   \\ \text{CHO} \\ \text{glucose} \end{array}$

crystals by treating with alcohol. A more practical method of preparing fructose consists in hydrolyzing inulin with dilute sulfuric acid. The excess sulfuric acid is eliminated by precipi-

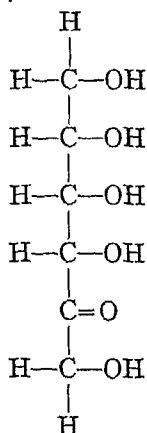
tating with barium hydroxide and filtering. Fructose is obtained by evaporating the filtrate. Inulin is a polysaccharide which occurs in dahlia tubers, artichokes, and other plants (page 269).

Fructose crystallizes in colorless needles. The anhydrous crystals obtained from its alcoholic solutions melt at  $95^{\circ}$ . It is sweeter than glucose and is converted by yeast into alcohol and carbon dioxide.

*Structure.* When treated with acetic anhydride and zinc chloride, it yields a pentacetyl derivative which shows the presence of five hydroxyl groups. When oxidized with nitric acid or bromine water, it yields a mixture of tartaric and glycolic acids, each of which contains a smaller number of carbon atoms than fructose:

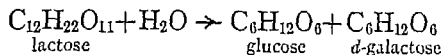


This reaction indicates that fructose has the structure of a ketone. When reduced with sodium amalgam, the hexahydroxyl alcohol *d*-sorbitol is obtained, which shows that fructose contains a straight chain of six carbon atoms. These facts show that fructose contains the ketone group ( $\text{C}=\text{O}$ ) and is a ketose having the structural formula,





**Other monosaccharides.** There are several other monosaccharides which have the formula  $C_6H_{12}O_6$  and are closely related to glucose and fructose. When lactose, or milk sugar,  $C_{12}H_{22}O_{11}$ , is hydrolyzed with dilute sulfuric acid, *d*-galactose and glucose are obtained:



*d*-Galactose is also obtained by the hydrolysis of other carbohydrates and by the oxidation of dulcitol, a hexahydroxyl alcohol which occurs in certain plants. It crystallizes in prisms melting at  $168^\circ$ . It is dextro rotatory and ferments with yeast.

*d*-Mannose,  $C_6H_{12}O_6$ , is obtained by oxidizing the hexahydroxyl alcohol mannitol with nitric acid. It may also be prepared from certain orchids and from seminine, a substance which occurs in certain plant seeds and in the shells of the vegetable ivory nut. It reduces Fehling's solution, is fermented by yeast, and is dextro rotatory. *d*-Galactose and *d*-mannose are aldoses.

*i*-Fructose,  $C_6H_{12}O_6$ , is a sugar which is obtained by the polymerization of formaldehyde. When an aqueous solution of formaldehyde containing calcium hydroxide is allowed to stand some time, a mixture of sugars having the composition  $C_6H_{12}O_6$  and known as *formose* is obtained:

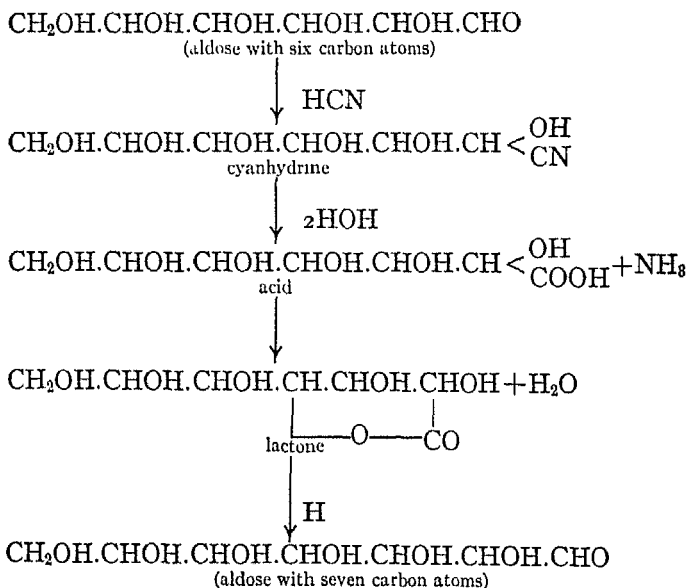


From this mixture E. Fisher isolated *i*-fructose.

*i*-Fructose is the racemic or (*d*+*l*) variety of fructose. It is inactive, and when fermented by yeast the *d*-fructose which it contains is decomposed into alcohol and carbon dioxide, while the *l*-fructose remains unchanged.

**Synthesis and decomposition of monosaccharides.** Various methods have been devised for preparing monosaccharides. The hydrolysis of polysaccharides such as cane sugar, which yields glucose and fructose, has already been referred to, as well

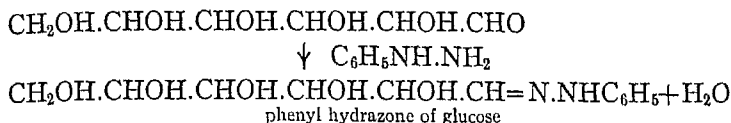
as the oxidation of hexahydroxy alcohols like *d*-sorbitol, which gives glucose, and the polymerization of formaldehyde, giving *i*-fructose. Of the other methods used for preparing monosaccharides the **hydrocyanic acid method** (Kiliani) is important because it enables us to prepare from one sugar another containing one more carbon atom. This method is based upon the reaction which takes place when aldehydes and ketones are treated with hydrogen cyanide. An aldose, for example, forms with hydrogen cyanide a cyanhydrine. The cyanhydrine when hydrolyzed yields an acid containing seven carbon atoms. When this acid loses water, it is converted into a lactone which, when reduced, yields an aldose:



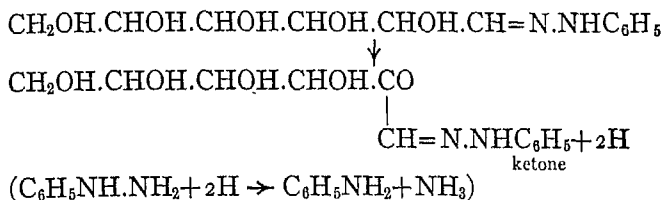
Thus from an aldose containing six carbon atoms we can prepare another aldose containing seven carbon atoms.

A method which has been used very successfully in investigating the constitution of monosaccharides is that based upon the

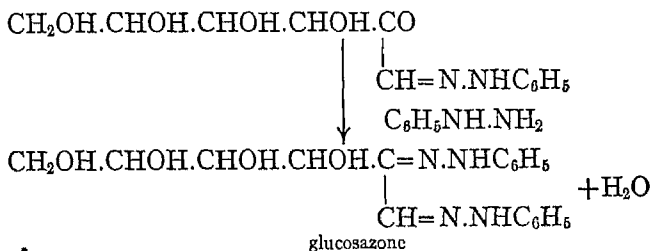
**phenyl hydrazine reaction** (E. Fisher). When an aldose or ketose sugar is treated with phenyl hydrazine, the products obtained are known as *phenyl hydrazones*. By treating glucose with phenyl hydrazine, the phenyl-hydrazone of glucose is obtained :



When an excess of phenyl hydrazine is employed, one of the (CHOH) groups of the hydrazone is oxidized, giving a ketone, and a molecule of phenyl hydrazine is reduced to aniline and ammonia :

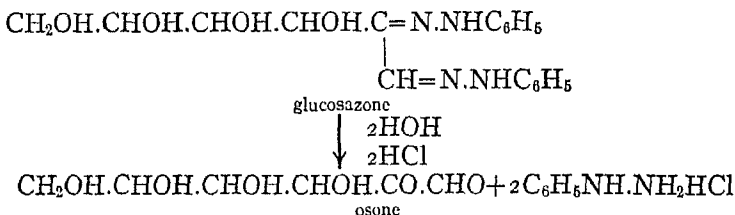


The ketone formed by the decomposition of the (CHOH) group of the hydrazone reacts with another molecule of phenyl hydrazine, giving an osazone of glucose known as *glucosazone* :

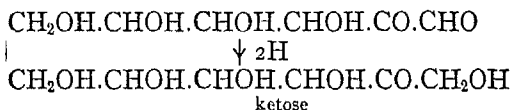


In a similar manner, when fructose is treated with phenyl hydrazine, it is decomposed, yielding the phenyl hydrazone of fructose. This then reacts with phenyl hydrazine, giving phenyl

fructosazone, which is identical with the osazone of glucose. The hydrazones are readily soluble in water, but the osazones are only difficultly soluble and therefore are very useful in enabling us to separate a certain sugar from a mixture. The osazones are decomposed by hydrogen chloride, yielding the hydrochloride of phenyl hydrazine and an osone:



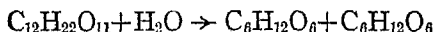
When the osone is reduced with zinc dust and acetic acid, it is converted into a ketose sugar:



As shown by the reactions above, an aldose may be converted into a ketose. An aldose, however, cannot be obtained from a ketose by this method.

**Polysaccharides which are sugars.** These substances consist mostly of disaccharides,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , such as cane sugar and lactose, and trisaccharides,  $\text{C}_{18}\text{H}_{32}\text{O}_{16}$ , like raffinose.

**Disaccharides.** A number of disaccharides occur naturally in certain plants, while others may be obtained by hydrolyzing certain polysaccharides (starch) which are not sugars. Some of them reduce Fehling's solution, while others do not. They are readily hydrolyzed into hexoses:



Since they have a molecular weight which is exactly double that of a hexose less one molecule of water, it would appear that

the disaccharides consist of a combination of two hexoses from which one molecule of water has been eliminated. If that is true, they might possibly be regarded, then, as the anhydrides of double hexoses. They cannot, however, be prepared by combining two hexoses in the presence of a dehydrating agent.

**Sucrose** (saccharose or cane sugar),  $C_{12}H_{22}O_{11}$ , is the most common variety of the disaccharides and the most important commercially. It occurs naturally in many different plants, such as sugar cane, sugar beets, sorghum, in the sap of the sugar maple, and in seeds such as walnuts, coffee, and almonds, and in honey and the blossoms of flowers.

**Manufacture of cane sugar** (sucrose). The commercial supply of sugar is obtained from sugar cane, which contains about 15 to 20 per cent of sucrose, and from sugar beets, which contain 7 to 17 per cent. The general process which is used to extract the sugar from the cane or beets is about the same in both cases, although the details are different. The process consists essentially in separating the juice from the vegetable fiber. The impurities in the juice, such as organic acids and albuminous substances, are precipitated. The purified juice thus obtained is evaporated and allowed to crystallize, after which the crystallized sugar is separated from the mother liquor or molasses.

In the commercial manufacture of sugar from sugar cane, the cane is cut near the base of the stem and crushed between heavy rolls or cylinders. The liquid thus expressed is known as *raw juice*, while the woody residue is called *bagasse*. Formerly the cane was crushed in primitive mills and about half the juice was lost. With modern machinery the total quantity of juice obtained represents about 90 per cent of the weight of the cane and contains 15 to 20 per cent of sugar. The raw juice thus obtained is treated with a solution of calcium hydroxide and heated until it boils. The lime precipitates the calcium salts of organic acids such as oxalic and citric acids. This removal

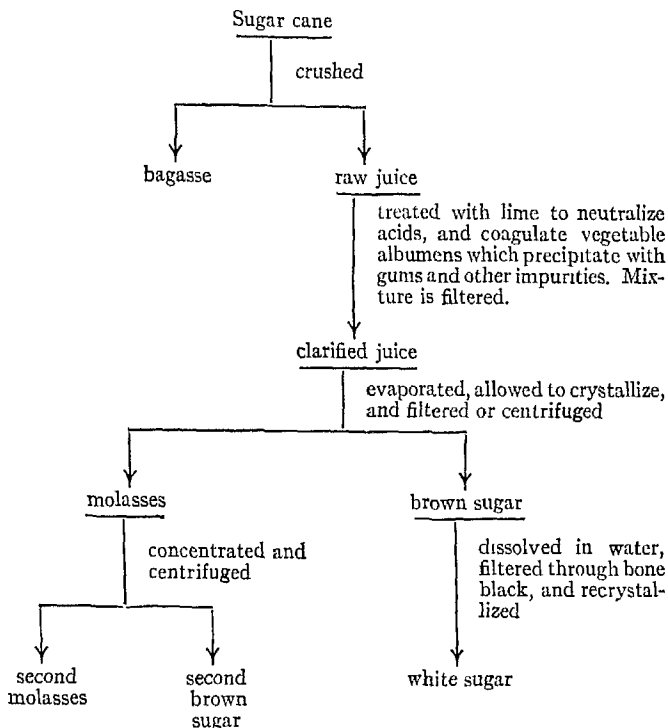
of acids prevents the sucrose from inverting into glucose and fructose. The lime also coagulates the vegetable albumens, which separate with gums and other impurities as a scum on the surface of the juice. As it is somewhat difficult to determine the exact amount of lime which is to be added, it is customary in some countries to add a slight excess of lime and precipitate the excess by passing carbon dioxide into the mixture. The juice is separated from the precipitated impurities and foreign matter by passing it through filter presses. The purified juice is concentrated by evaporating in vacuum pans. The sugar which crystallizes when the syrup is cooled is separated from the mother liquor, or molasses, by centrifugal machines. The centrifugals, which resemble a drum-shaped sieve, are made to revolve rapidly, with the result that the liquid molasses is thrown by centrifugal force through the small openings of the sieve, while the sugar crystals remain behind. The product thus obtained is a brown sugar, which may be converted into white granulated sugar by a refining process which consists essentially in dissolving the brown sugar in water and filtering through bone black to decolorize it. The solution of clarified sugar thus obtained is evaporated in vacuum pans and recrystallized.

The molasses that is separated from the sugar still contains about 50 per cent of sugar. This is further concentrated by boiling in vacuum pans and by centrifuging. This yields a second sugar, which is rather yellow, and a second molasses. The second molasses, which contains about 40 per cent of sugar, is fermented into rum, or alcohol, or is used as cattle food. The first molasses is also used as a table syrup and in cooking. A brief outline of this process which is used for the manufacture of cane sugar is given on the following page.

Sugar is manufactured from beets by the diffusion process. This consists in cutting the beets into small pieces by machinery and digesting the pieces with warm water, which dissolves out the crystallizable sugar, leaving the colloids such as albumi-

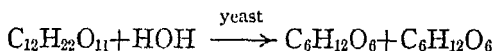
nous substances and gums. The sugar solution thus obtained is treated in a manner quite similar to that employed in preparing sugar from the juice of the sugar cane.

## MANUFACTURE OF CANE SUGAR



Sucrose is very soluble in water, from which it crystallizes in large, transparent prisms known as *rock candy*. It melts at  $160^{\circ}$  and when cooled solidifies as a white, glassy mass which becomes crystalline when allowed to stand. When heated to a temperature of about  $200^{\circ}$  it loses water, becomes brown in color, and is converted into a brown mass called *caramel*, which is used considerably as a flavoring and coloring material for

food products. When sucrose is heated to a higher temperature, gases are evolved and a residue of sugar charcoal remains. Sucrose is oxidized readily by strong oxidizing agents. Chromic acid or potassium chlorate react with sucrose with explosive violence. The interaction of concentrated nitric acid and sucrose yields oxalic acid, oxides of nitrogen, and other products. Unlike glucose, a solution of sucrose does not become brown in color when treated with a solution of caustic alkali. Sucrose chars when treated with concentrated sulfuric acid. It is dextro rotatory,  $[\alpha]_D^{20} = +66.5^\circ$ . Sucrose combines with various oxides and hydroxides of metals such as calcium, barium, and strontium, forming sucrates. Several sucrates of calcium, such as  $C_{12}H_{22}O_{11} \cdot CaO \cdot 2H_2O$ , have been isolated. Strontium sucrate,  $C_{12}H_{22}O_{11} \cdot SrO \cdot H_2O$ , is used in certain processes to separate sucrose from molasses. These sucrates are readily prepared by adding to the sucrose solution a solution of the metallic hydroxide. They may be decomposed by carbon dioxide into sucrose and the carbonate of the metal. Pure sucrose does not reduce Fehling's solution. When treated with yeast which contains the enzyme invertase, sucrose ferments and is inverted, or decomposed, into glucose and fructose:



#### EXPERIMENT 54

##### Behavior of sucrose with Fehling's solution

Dissolve about 0.5 gram of white crystallized cane sugar in 4 cc. of water. Add about 3 cc. of Fehling's solution and boil. Is the Fehling's solution reduced?

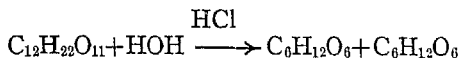
Sucrose is hydrolyzed by dilute solutions of mineral acids, such as hydrochloric or sulfuric, yielding invert sugar, which consists of equal quantities of dextrose and levulose. Both glucose and fructose reduce Fehling's solution.



## EXPERIMENT 55

## Hydrolysis of sucrose

In a 200 cc. Erlenmeyer flask dissolve 3 grams of pure sucrose in 40 cc. of water. Add 0.5 cc. of concentrated hydrogen chloride. Heat the solution on a water bath about 40 minutes. Neutralize about 2 cc. of this solution with sodium carbonate solution (1:10), and test with Fehling's solution:



Many plants and fruits contain also, in addition to sucrose, glucose and fructose. These substances, therefore, give a positive reaction when tested for invert sugar with Fehling's solution.

## EXPERIMENT 56

## Test for invert sugar in bananas

Cut a piece of ripe banana about the size of a penny. Place in a mortar, add 10 cc. of water, and grind with a pestle. Pour into a beaker, and add 30 cc. of water. Test with litmus, and if acid, neutralize with dilute sodium carbonate solution. Filter, and test a few cubic centimeters of the filtrate with Fehling's solution. Is the Fehling's solution reduced?

The practical determination of the strength of a given sugar solution is made with a special kind of polariscope known as a *saccharimeter*. There are various kinds of saccharimeters. The German (Schmidt and Haench) instrument, for instance, contains a lower saccharimeter scale and an upper vernier scale. It is so constructed that the 100° reading on the lower saccharimeter scale is obtained by using a 20 cm. tube containing pure sucrose (cane sugar) solution, which is prepared by dissolving 26 grams of pure cane sugar in distilled water and diluting to a volume of 100 cc. at 20°. The saccharimeter scale extends from 0° to -30° on the negative side of the scale and from 0° to +100° on the positive side. The number of degrees' rotation on the lower saccharimeter scale is indicated by the zero of the

upper vernier scale, and the fractional part of a saccharimeter scale division is shown by that division of the vernier scale which coincides with a division on the saccharimeter scale.

## EXPERIMENT 57

### Polarization of cane sugar

Weigh in a sugar dish, or 100 cc. evaporating dish, 26 grams of brown cane sugar. Add about 20 cc. of hot water and grind the mixture with a pestle until the sugar is dissolved. With the aid of a wash bottle wash the pestle, allowing the drippings to run into the sugar solution. The sugar solution is now poured through a funnel into a 100 cc. flask. Wash the evaporating dish, allowing the wash water to run into the flask containing the sugar solution. Allow the flask to cool to the room temperature, and add 5 cc. of lead subacetate solution. Dilute the mixture with water to the 100 cc. mark. Shake the mixture thoroughly, taking care that none of the liquid is lost, so that a change in volume is caused. Filter through a folded filter. Fill a 20 cm. polarizing tube with a portion of the filtrate.

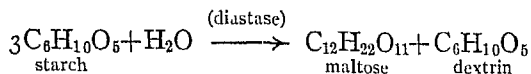
The polarization reading is now obtained in the following manner: Adjust the saccharimeter scale to the zero reading. If the instrument is correct, a zero reading will give a field of uniform color. Place the sugar solution in the saccharimeter, and observe that the field is no longer uniform. Continue to observe the field, and turn the scale until a uniform field is again obtained. A second reading is now taken. The result of the second reading represents the number of degrees of rotation, or the polarization reading.

A polarization reading does not represent the exact purity of a sample of brown sugar, since such a sugar contains a large percentage of sucrose which rotates the plane of polarization to the right, together with small amounts of other substances such as glucose, which rotates to the right, or fructose, which rotates to the left. However, a polarization reading does give an approximate idea of the purity of a sample of sugar.

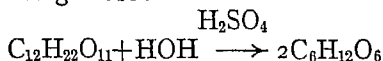
*NOTE.* Lead subacetate solution is prepared by boiling 430 grams of normal lead acetate with 130 grams of litharge and 1000 cc. of water for 0.5 hour. The mixture is allowed to cool and settle, after which it is filtered and diluted to a specific gravity of 1.25 with water which has been boiled recently. The stock room supplies this solution.

**Structure.** When sucrose is treated with acetic anhydride, an octacetate having the formula  $C_{12}H_{14}O_3(CH_3COO)_8$  is obtained. The reaction shows that sucrose contains eight hydroxyl groups. Sucrose does not react with phenyl-hydrazine or with Fehling's solution, a behavior which indicates the absence of aldehyde or ketone groups. The fact that it yields dextrose and levulose when hydrolyzed would seem to indicate that it consists of a combination of dextrose and levulose from which one molecule of water has been eliminated.

**Maltose**,  $C_{12}H_{22}O_{11}$ , is produced by the action of malt on starch :



This reaction is produced by the enzyme diastase which the malt contains. Since the formula of starch is a multiple of  $C_6H_{10}O_5$ , the reaction above is really more complex than the equation would seem to indicate. Maltose is obtained commercially as an intermediate product in the manufacture of alcohol and alcoholic beverages. It is very soluble in water and crystallizes in needles with one molecule of water. It has a strong dextro rotation,  $[\alpha]_D^{20} = 137^\circ$ . It reduces Fehling's solution, and ferments with yeast, yielding alcohol and carbon dioxide. When hydrolyzed with a dilute solution of sulfuric acid, it is converted into glucose :

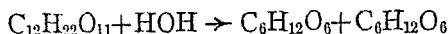


It reacts with phenyl hydrazine, yielding an osazone, and when treated with acetic anhydride gives an octacetate.

**Lactose** (milk sugar),  $C_{12}H_{22}O_{11}$ , occurs in the milk of mammals to the extent of about 4 per cent and is obtained as a by-product in the manufacture of cheese. When milk is treated with rennet, the casein and fats are precipitated. These are separated from the aqueous solution known as *whey*. Milk sugar is obtained as crystals from the whey by evaporation. Rennet is obtained

from animal bodies. It is a mixture of enzymes such as the gastric rennin, which is present in the gastric juice.

Lactose crystallizes with one molecule of water and is not as sweet as sucrose. It reduces Fehling's solution, but less rapidly than glucose. It is converted into lactic acid by the lactic acid ferment and is hydrolyzed by dilute acids into glucose and galactose, which are aldoses having the formula  $C_6H_{12}O_6$ :



Lactose is dextro rotatory and when heated to  $140^\circ$  becomes anhydrous.

**Trisaccharides.** Raffinose,  $C_{18}H_{32}O_{16}$ , is the only member of this group of any special importance. It occurs in sugar beets, cotton seed, and barley, and may be prepared from the molasses obtained in the manufacture of sugar from beets. It crystallizes with five molecules of water, which are lost at  $100^\circ$ . The anhydrous sugar melts at  $118^\circ$ . It is dextro rotatory and does not reduce Fehling's solution.

The more important monosaccharides and polysaccharides which are sugars are given in the table on the opposite page. There are also included the important polysaccharides which are not sugars.

**Polysaccharides which are not sugars.** The members of this group are complex substances of high molecular weights. Their composition is represented by the formula  $C_6H_{10}O_5$ , and since their molecular weights are unknown it is customary to represent these substances by the formula  $(C_6H_{10}O_5)_n$ . Since they yield monosaccharides and disaccharides when hydrolyzed, their molecules would seem to consist of combinations of the simpler carbohydrates with the elimination of water.

**Starch** (amylum),  $(C_6H_{10}O_5)_n$ , occurs in many different kinds of plants, in all kinds of grain such as wheat and rice, and in potatoes, arrowroot, and other tubers. The flour obtained by grinding wheat contains about 65 per cent of starch. Rice flour

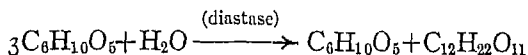
## CARBOHYDRATES

CLASSES	NAME	MOLECULAR FORMULA	STRUCTURAL FORMULA
Monosaccharides	Glycolic aldehyde	$C_2H_4O_2$	$\begin{array}{c} CH_2OH \\   \\ CHO \end{array}$
	Glyceric aldehyde	$C_3H_6O_3$	$\begin{array}{c} CH_2OH \\   \\ CHOH \\   \\ CHO \end{array}$
	Dihydroxy acetone	$C_3H_6O_3$	$\begin{array}{c} CH_2OH \\   \\ CO \\   \\ CH_2OH \end{array}$
	Erythrose	$C_4H_8O_4$	$\begin{array}{c} CH_2OH \\   \\ (CHOH)_2 \\   \\ CHO \end{array}$
	Arabinose	$C_5H_{10}O_5$	$\begin{array}{c} CH_2OH \\   \\ (CHOH)_3 \\   \\ CHO \end{array}$
	Xylose		$\begin{array}{c} CH_2OH \\   \\ (CHOH)_3 \\   \\ CHO \end{array}$
	Glucose	$C_6H_{12}O_6$	$\begin{array}{c} CH_2OH \\   \\ (CHOH)_4 \\   \\ CHO \end{array}$
	Galactose		$\begin{array}{c} CH_2OH \\   \\ (CHOH)_4 \\   \\ CHO \end{array}$
	Mannose		$\begin{array}{c} CH_2OH \\   \\ (CHOH)_4 \\   \\ CHO \end{array}$
	Fructose	$C_6H_{12}O_6$	$\begin{array}{c} CH_2OH \\   \\ (CHOH)_3 \\   \\ CO \\   \\ CH_2OH \end{array}$
Disaccharides	Sucrose	$C_{12}H_{22}O_{11}$	
	Maltose		
	Lactose		
Trisaccharides	Raffinose	$C_{18}H_{32}O_{16}$	
Polysaccharides which are not sugars	Starch	$(C_6H_{10}O_5)_n$	
	Cellulose		
	Dextrin		

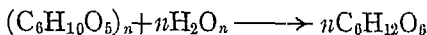
yields about 75 per cent and rye about 70 per cent of starch. The flour from which bread is made consists, therefore, largely of starch. Starch is manufactured from potatoes, wheat, rice, corn, and arrowroot. The manufacture of starch consists essentially in separating it from the gluten, oil, albuminous matter, and other substances which are present in the material used in preparing the starch. In the manufacture of starch from corn, the grain is soaked in warm water for several days. It is then ground in a mill through which a stream of water is allowed to run continuously. The water carries the starch away as a milky liquid to strainers made of bolting cloth. The milky liquid containing the starch passes through the cloth strainer and is allowed to settle, after which the water is drawn off. The white sediment is again treated with water and stirred up. This allows the gluten to settle, while the starch remains suspended in solution. The starch solution is drawn off into another tank and allowed to settle. This process is repeated several times to separate the starch from the gluten, after which the starch is washed with water and allowed to dry at a low temperature. The gluten obtained as a by-product may be used as cattle food.

Starch is used extensively as food and for other purposes, such as the preparation of glucose and paste and in laundry work. Starches obtained from different sources vary somewhat in their properties. Wheat starch is especially adapted for making paste. Starch from arrowroot is useful in laundry work; sago and tapioca starch are used chiefly as foods. Rice starch is best adapted for toilet powders, while potato and corn starch are used largely in the preparation of glucose. Starch is a white powder consisting of microscopic granules which vary in appearance and size, depending upon the plants from which the starch is obtained. Starch is insoluble in cold water. The starch granules are surrounded by a cellulose membrane, and when starch is heated with water the granules swell up and burst. When treated with cold dilute hydrogen chloride for some

days, it is converted into a variety of starch which is soluble. At about  $225^{\circ}$  it is converted into dextrin. It does not ferment or react with phenyl hydrazine and is not reduced by Fehling's solution. It is hydrolyzed by acids and enzymes. When treated with malt extract which contains the enzyme diastase, starch is converted into dextrin and maltose at a temperature of about  $65^{\circ}$ :



When hydrolyzed with dilute acids, it is converted into dextrin,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , which on further hydrolysis yields glucose:



Although the formulas of starch and dextrin,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , are written in the same manner, it is obvious that the value of  $(n)$  in the dextrin formula must be much less than in the starch formula, since dextrin may be obtained by the decomposition of starch.

Starch is detected by the intense blue color which it gives with a solution of iodine.

#### EXPERIMENT 58

##### Preparation of starch solution

Prepare a starch solution in the following manner: Pour 150 cc. of water into a beaker, heat until it boils, and then remove the flame. Place about a gram of starch in a mortar, add about 20 cc. of water, and grind the mixture with a pestle. The starch mixture is now poured into the boiling water and the liquid stirred, cooled, and allowed to settle. Use the clear supernatant liquid for Experiments 59 and 61.

#### EXPERIMENT 59

##### Test for starch

Prepare a potassium iodide solution of iodine in the following manner: Dissolve about a gram of powdered potassium iodide in 10 cc. of water. Add to this solution a few crystals of powdered iodine, and shake.

Add a few drops of this dark-colored iodine solution to 3 cc. of the cold starch solution previously prepared (Experiment 58). A deep-blue coloration is produced immediately. (The remainder of the potassium iodide solution of iodine should be laid aside for Experiment 60.)

Boil 5 cc. of the starch solution (Experiment 58) with a few cubic centimeters of Fehling's solution, and notice if there is any reduction.

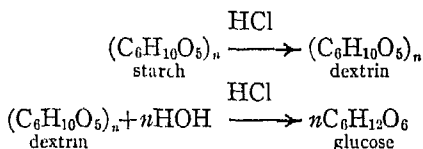
## EXPERIMENT 60

### Test for starch in potatoes

Place a small piece of white potato about the size of a penny in a mortar, and add 4 cc. of water. Grind the mixture with a pestle; add about 10 cc. of water, and a few drops of a potassium iodide solution of iodine (Experiment 59).

## EXPERIMENT 61

### Hydrolysis of starch



Pour 40 cc. of starch solution (Experiment 58) into an Erlenmeyer flask, and add 4 cc. of concentrated hydrogen chloride. Place the flask on a boiling water bath, and heat 1 hour. Pour a portion of the solution into a beaker, and neutralize with sodium carbonate solution. A few cubic centimeters of the neutralized solution is now introduced into a test tube and tested with Fehling's solution. In the presence of hydrogen chloride the starch is converted into dextrin,  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , which is further hydrolyzed to glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ .

**Glycogen** (animal starch),  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , is a carbohydrate which occurs in the liver, muscles, and blood, and in certain fungi. It is a white powder which gives an opalescent solution with water. It is dextro rotatory and gives a red color with iodine. It does not ferment with yeast, or reduce Fehling's



solution. When hydrolyzed with dilute acids, it is converted into glucose. It is broken down in the animal body, yielding glucose.

**Inulin**,  $(C_6H_{10}O_5)_n$ , is a white powder which resembles starch and occurs in potatoes, dahlia tubers, artichokes, and other plants. Solutions of inulin are levo rotatory and are not colored by iodine. It is hydrolyzed by dilute acids, yielding fructose.

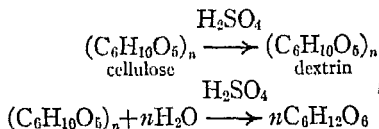
**Dextrin**,  $(C_6H_{10}O_5)_n$ , is produced by heating starch and by the acid hydrolysis of starch. The different varieties of dextrin are transparent amorphous substances. The gloss which is produced on starched fabrics by ironing is due to the formation of transparent dextrins. Dextrin is soluble in water, from which it is precipitated by alcohol. Solutions of dextrin reduce Fehling's solution and are dextro rotatory. When dextrin is dissolved in water, it forms a thick, gummy syrup which is used as a substitute for natural gum. Dextrin solutions are used for making mucilage and are also employed in confectionery and in thickening tanning extracts.

**Cellulose**,  $(C_6H_{10}O_5)_n$ , is the principal constituent of the cell membranes and tissues of all plants. Cellulose may be separated from the other substances, such as lignin and resins, with which it occurs, by treating it with certain reagents which do not affect the cellulose but dissolve the other substances which are present.

Cellulose is a very stable substance and is insoluble in most of the ordinary solvents. It is dissolved by Schweitzer's reagent, which is an ammoniacal solution of copper hydroxide. It is precipitated from this solution, by the addition of acids, as a jelly which, when washed with water and dried, is converted into a white amorphous powder. Cellulose is also dissolved by concentrated sulfuric acid. When this acid solution of cellulose is diluted with water and boiled, the cellulose is converted into dextrin, which is further hydrolyzed into glucose.

## EXPERIMENT 62

## Hydrolysis of cellulose



Place about twenty small pieces of filter paper (the size of a penny) in a mortar, and dissolve them in sulfuric acid by adding the acid a few drops at a time and grinding the mixture with a pestle. Pour about 20 cc. of water into an Erlenmeyer flask and add the acid solution of cellulose. Place the flask on a boiling water bath and allow it to remain there 0.5 hour. Add about 20 cc. of water, and filter. Neutralize 5 cc. of the filtrate with dilute sodium carbonate solution (1:5) and test with Fehling's solution.

**Commercial products from cellulose.** As many useful and valuable commercial products may be prepared from cellulose, it is one of the most important of the carbohydrates. The fiber obtained from the cotton plant is manufactured into cotton cloth. The fiber of flax is converted into linen cloth, and hemp fiber is used in making hemp twine and ropes.

**Paper.** The various grades of paper consist almost entirely of cellulose. Paper is manufactured from cellulose, which is obtained from various sources, such as cotton and linen rags, wood fibers, and old ropes. Paper which is to be used for newspapers, books, and writing paper is prepared almost entirely from various kinds of woods, such as pine, poplar, beech, birch, and spruce. The logs of wood are cut into small pieces and ground in a mill, through which water is sprayed to prevent heating and to remove the woody fibers. The wood pulp thus obtained is treated with various reagents, such as sodium hydroxide or the acid sulfites of calcium or magnesium, which decompose the foreign matter combined with the cellulose. The cellulose thus freed from foreign matter is washed, after which it is worked into paper by a machine which is so constructed that a thin layer of pulp is allowed to pass through various rolls.

These rolls press out the water and convert the pulp into sheets of paper, which are wound into paper rolls.

The best grades of filter paper consist of almost pure cellulose, with only a trace of impurities. This kind of filter paper is obtained by treating ordinary filter paper with hydrofluoric acid to remove traces of silica. It is then washed with water and dried at  $100^{\circ}$ .

**Artificial silk** is manufactured from wood pulp by treating it with a suitable solution, such as calcium hydrogen sulfite under pressure, to remove the foreign matter (gums, oils, resins, etc.). The purified cellulose is dissolved by treating it with Schweitzer's reagent or by converting it into soluble nitrates or acetates of cellulose. The cellulose solution thus obtained is forced through capillary tubes into a liquid which reprecipitates the cellulose or its derivatives. The precipitate is thus obtained in the form of fine threads, or fibers, which may be converted into cloth or fabrics. The material thus obtained resembles silk and is known commercially as *artificial silk*. It has a silky luster and can be dyed readily, but it is not as strong and durable as natural silk.

**Mercurized cotton** is the material obtained by treating ordinary cotton with a solution of sodium hydroxide. By this treatment the cellulose of the cotton is converted into cellulose hydrates and the cotton becomes somewhat transparent, resembles silk in appearance, possesses greater strength than ordinary cotton, and takes dyes more readily.

**Explosives, celluloid, and other products from cellulose.** When cellulose is nitrated with a mixture of nitric and sulfuric acids, nitrates of cellulose (nitrocellulose) such as the di-, tri-, and tetranitrates are obtained, depending upon the quantity, concentration, and length of time required to effect the nitration. Guncotton, or pyroxylin, contains the higher nitrates of cellulose (penta- and hexanitrates). Pyroxylin burns very rapidly without giving off smoke and explodes with extreme violence

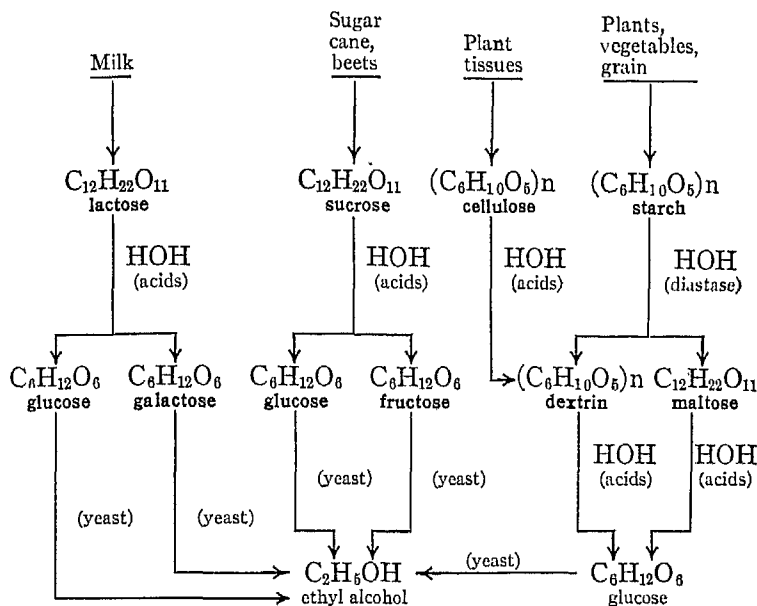
when struck. It is the active constituent of certain of the smokeless powders and is used extensively as an explosive. The lower nitrates of cellulose, known as *soluble guncotton*, are soluble in alcohol and ether. This alcohol ether solution of soluble guncotton is known as *collodion* and is used in surgery and photography, and in the production of artificial silk filaments. Celluloid is obtained by dissolving nitrated cellulose in molten camphor. Although it is very inflammable, it is not explosive and is used in the manufacture of a variety of small articles for ornament or toilet purposes. Cordite is a mixture of nitroglycerin and nitrocellulose dissolved in a mixture of acetone and vaseline. This too is used as a smokeless powder.

As previously stated, when cellulose is dissolved in concentrated sulfuric acid and the solution is diluted with water and boiled, the cellulose is converted into dextrin, which is further hydrolyzed into glucose. Since glucose may be converted into alcohol, it is evident that paper, wood, rags, and other substances which consist largely of cellulose might be used for the manufacture of alcohol.

**Gums** are usually complex mixtures obtained from plants. These sticky mixtures contain certain carbohydrates. Many of them yield pentoses or hexoses when hydrolyzed. Gum arabic is obtained from the bark of acacia trees in Senegambia. It is soluble in water and is used in pharmacy in preparing emulsions. It is also used in making mucilage, and for other purposes. Gum arabic and the gums obtained from peach and cherry trees yield arabinose when hydrolyzed. Agar-agar, obtained from seaweed, yields galactose when hydrolyzed. Wood gum, obtained from jute, beech wood, and certain other woods, yields xylose when hydrolyzed with dilute acids.

**Enzymes.** In discussing the preparation of ethyl alcohol from cane sugar by the fermentation process (page 78), attention was called to the fact that this action is brought about by the presence in the yeast of two enzymes. One of these en-

## CARBOHYDRATES



zymes, known as *invertase*, converts the cane sugar into glucose and fructose, while the other, called *zymase*, changes these simpler sugars into alcohol and carbon dioxide. Many of the chemical changes which occur naturally in plants and animals are produced by enzymes, and they are, therefore, substances of considerable importance. These enzymes are products of a living cell such as the yeast plant and act catalytically in chemical reactions. Formerly it was thought that fermentation reactions were caused by living organisms, but the present view is that these changes are caused by enzymes, which are complex substances occurring naturally in certain bacteria, molds, yeast, and living tissues. These enzymes are able to bring about various chemical changes such as the splitting of complex compounds into simpler ones, as in the conversion of cane sugar

into dextrose and levulose by invertase. Among other chemical changes which are effected by enzymes are hydrolysis (conversion of starch into glucose by diastase) and oxidation reactions (fermentation of ethyl alcohol to acetic acid and lactose to lactic acid). Certain of the enzyme reactions may also be effected by ordinary chemical means, as in the acid hydrolysis of cane sugar and the oxidation of alcohol to acetic acid.

#### QUESTIONS

1. Name, with formulas, the general classes of carbohydrates.
2. What is meant by the terms "triose," "tetrose," and "hexose"?
3. What is invert sugar, and how is it obtained? Why is it called invert sugar?
4. Name some of the substances from which glucose may be obtained.
5. How is glucose obtained from corn?
6. For what purposes is glucose used?
7. How is Fehling's solution affected by glucose?
8. What is Fehling's solution? For what purpose is it used? Why is it alkaline, and why does it contain Rochelle salt?
9. How is the structure of glucose determined?
10. From what hydrocarbon is glucose derived?
11. Write the structural formula of an aldose and of a ketose.
12. Explain how an aldose containing seven carbon atoms can be prepared from another aldose containing six carbon atoms.
13. Explain how an aldose can be converted into a ketose.
14. What are disaccharides?
15. From what substances is the commercial supply of cane sugar obtained?
16. Explain how cane sugar is manufactured from sugar cane.
17. How is cane sugar affected by yeast?
18. Does pure cane sugar reduce Fehling's solution?
19. Explain, with equation, the acid hydrolysis of sucrose. How are the products of this reaction tested?
20. How do you test for invert sugar in bananas?
21. Explain how the polarization of a sugar solution is determined.
22. How are maltose and lactose obtained?
23. From what substances is starch obtained?
24. For what purposes is starch used?
25. How do you test for starch?
26. Explain, with equations, the acid hydrolysis of starch. How are the products tested?
27. What is cellulose?
28. Explain the hydrolysis of cellulose. How is the product tested?
29. Name some of the commercial products obtained from cellulose.
30. Write outline equations showing how alcohol can be obtained from lactose, sucrose, cellulose, or starch.
31. What are enzymes?

## AROMATIC COMPOUNDS





## CHAPTER SEVENTEEN

### AROMATIC HYDROCARBONS

**Introduction.** As previously stated, organic compounds are usually classed in two divisions, the aliphatic hydrocarbons and derivatives and the aromatic hydrocarbons and derivatives. The substances which we have considered in the preceding chapters are aliphatic compounds, which are derived from the paraffins and related hydrocarbons. We are now going to study a large group of substances known as the aromatic compounds, which constitute the second main division of organic compounds. Many of the dyestuffs, drugs, and pharmaceutical and medicinal preparations are members of this group, which is, therefore, one of unusual interest and importance. These substances are usually called the *aromatic compounds* because many of them have a fragrant, aromatic odor. In certain respects the aromatic compounds are quite different from the aliphatic compounds. The aromatic compounds are regarded as derivatives of the hydrocarbon benzene,  $C_6H_6$ , from which they may be obtained either directly or indirectly, and all the aromatic compounds contain six or more carbon atoms. Aliphatic compounds with but few exceptions are represented by formulas which have an open chain of carbon atoms, while the aromatic compounds are represented by formulas which have a closed chain, or ring, of carbon atoms. For these and other reasons the aromatic compounds are classified as a separate division of organic compounds.

**Sources of aromatic compounds (coal tar).** Although some of the aromatic compounds may be obtained from plants, the principal source is coal tar. Coal tar is a thick, black, oily liquid and is obtained as a by-product in the manufacture of illuminating gas from bituminous coal. Illuminating gas is manufactured by distilling coal in large clay or iron retorts.

The coal is decomposed, yielding a variety of volatile products and a residue of coke, which is a non-volatile, porous mass of impure carbon. The coke is used as fuel. The distillate, consisting of hot volatile products, is conducted through a series of pipes called *condensers*, which are cooled by water. It consists principally of three products: illuminating gas, a liquid containing ammonia, and coal tar. The illuminating gas, which is a mixture of methane, hydrogen, carbon monoxide, and other gases, together with impurities, is conducted into a suitable apparatus for purification, after which it is led into large gas holders, where it is stored for future use. The ammoniacal liquid and coal tar which separate out in the condensers are conducted into large tanks and allowed to settle. They separate into layers. The top layer consists of the ammoniacal liquor from which the commercial supply of ammonia and ammonium salts is obtained. The bottom layer is coal tar.

#### EXPERIMENT 63

##### Preparation of coal tar and illuminating gas

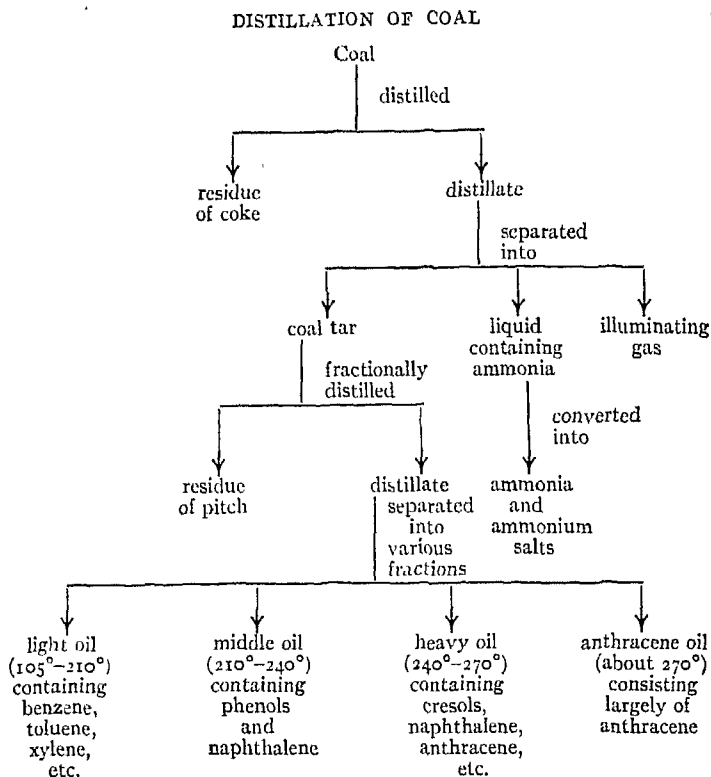
*Procedure.* Place about 15 grams of coarsely powdered coal which contains no moisture in a hard glass test tube. The test tube is now clamped to an iron stand, and into the open end is placed a cork stopper which contains a glass tube drawn out to a fine opening. The test tube is now heated; gases are evolved, leaving a black residue. Ascertain if the gases are combustible. What is the black residue?

NOTE. Most of the moisture is removed from the coal by placing the coal in an evaporating dish and heating in an air bath at a temperature of  $120^{\circ}$  for about an hour. The coal is then placed in a bottle, which is stoppered securely and set aside until ready for use.

Coal tar is used somewhat for such purposes as preserving wood and preparing tar paper. It yields a number of valuable constituents, such as naphthalene, anthracene, carbolic acid, and the aromatic hydrocarbons of the benzene series. It is there-

fore a product of considerable commercial importance. The coal tar is separated commercially into its valuable constituents by fractional distillation. The first fraction, collected at  $105^{\circ}$ , consists largely of water, ammonium salts, and volatile oils. The second fraction, collected between  $105^{\circ}$  and  $210^{\circ}$ , consists of light oil which contains the aromatic hydrocarbons benzene, toluene, xylenes, small quantities of carbolic acid, and other substances. The third fraction ( $210^{\circ}$ – $240^{\circ}$ ) contains carbolic acid, other phenols, and naphthalene. The fourth fraction ( $240^{\circ}$ – $270^{\circ}$ ) contains creosote oils, which consist largely of cresols, naphthalene, and other substances. Anthracene oil, consisting largely of anthracene, distils over above  $270^{\circ}$ , and the residue remaining in the still consists of pitch. The crude distillates obtained from the coal tar are further purified by continued fractional distillation and other means. The fraction ( $105^{\circ}$ – $210^{\circ}$ ) containing the light oil is treated with sodium hydroxide, which removes the carbolic acid, and with sulfuric acid, which removes pyridine and other basic substances. It is washed with water after each treatment, after which it is again subjected to fractional distillation. The first fraction, boiling between  $82^{\circ}$  and  $110^{\circ}$ , consists largely of benzene and toluene. The second fraction ( $110^{\circ}$ – $140^{\circ}$ ) consists of benzene, toluene, and the xylenes. The third fraction, above  $140^{\circ}$ , consists largely of the xylenes, mesitylene, etc., and is used as a solvent for resins and rubber. By further methods of purification the individual members of the benzene series of hydrocarbons, such as benzene, toluene, and the xylenes, may be obtained in fairly pure condition.

A brief outline showing the principal products obtained by distilling coal is given in the following table :



There are several series of aromatic hydrocarbons, but as the members of the benzene series are the simplest of the aromatic hydrocarbons, we shall begin our study of aromatic compounds by considering a few of the simpler members of this series and some of their derivatives.

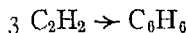
**Benzene**, (benzol)  $C_6H_6$ , is the simplest of the aromatic hydrocarbons and may be regarded theoretically as the starting point from which all other aromatic hydrocarbons may be derived. Benzene was discovered in 1825 by Faraday in a liquid which he obtained by compressing coal gas. It is manufactured

commercially, as previously described, from the light oil obtained from coal tar. It may be prepared in the laboratory from benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , by heating the sodium salt of benzoic acid,  $\text{C}_6\text{H}_5\text{COONa}$ , with soda lime:



This reaction is similar to that used in preparing methane and other aliphatic hydrocarbons (Experiment 9, page 23).

Benzene may be prepared also by passing acetylene gas through a tube heated to dull redness:



As shown by the reaction above, the benzene is thus obtained by the polymerization of acetylene. This is theoretically an important synthesis of benzene. Since acetylene can be obtained by the direct combination of hydrogen and carbon, the above synthesis shows how benzene could be prepared from the elements. Furthermore it shows how an aromatic compound may be obtained from an aliphatic compound. Benzene may be prepared also from phenol,  $\text{C}_6\text{H}_5\text{OH}$ , and aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ . These methods will be described later.

#### BENZENE SERIES

NAME	MOLECULAR FORMULA	ABBREVIATED STRUCTURAL FORMULA
Benzene	$\text{C}_6\text{H}_6$	$\text{C}_6\text{H}_6$
Toluene	$\text{C}_7\text{H}_8$	$\text{C}_6\text{H}_5\text{CH}_3$
Xylene	$\text{C}_8\text{H}_{10}$	$\text{C}_6\text{H}_4(\text{CH}_3)_2$
Mesitylene	$\text{C}_9\text{H}_{12}$	$\text{C}_6\text{H}_3(\text{CH}_3)_3$
Durene	$\text{C}_{10}\text{H}_{14}$	$\text{C}_6\text{H}_2(\text{CH}_3)_4$

Benzene is a colorless liquid which boils at  $80.4^{\circ}$ . Like many other aromatic compounds it has a somewhat pleasant aromatic odor. It has a specific gravity of 0.899 at  $0^{\circ}$ . It is lighter than water, is inflammable, and burns with a luminous, smoky flame. When cooled in a freezing mixture of ice and water, it separates in crystals which melt at  $5.4^{\circ}$ . It may therefore be purified by simply allowing it to crystallize at a low temperature, filtering, and discarding the impure liquid which does not crystallize. It is soluble in alcohol, chloroform, and ether but insoluble in water. As benzene dissolves fats and resins readily, it is used as a solvent and for cleaning purposes. Its principal use, however, is for the manufacture of nitrobenzene and other aromatic compounds.

#### EXPERIMENT 64

##### Reactions of benzene, $C_6H_6$

*A.* Pour 1 cc. of benzene on a small watch glass and set fire to it. Does it burn readily?

*B.* Pour 5 cc. of benzene into a test tube and immerse it in a mixture of ice and water. Does it crystallize? Could benzene be purified by fractional crystallization?

*C.* In a test tube shake 2 cc. of benzene with a dilute rose-colored solution of potassium permanganate which has been made alkaline by means of a dilute solution of sodium carbonate (1:10). Is the permanganate solution decolorized immediately? Compare results with Experiment 13 *C* (page 61).

*D.* Pour 2 cc. of benzene into a test tube and add a few drops of a 5 per cent solution of bromine dissolved in carbon tetrachloride. Is the bromine solution decolorized immediately? Note the result and compare with Experiment 13 *D* (page 62).

**Reactions of benzene.** Benzene is a very stable compound. It is not acted upon readily by oxidizing agents. When heated with solutions of extremely energetic oxidizing agents such as chromic acid or potassium permanganate, it is only very slowly decomposed. A solution of alkaline potassium permanganate, for instance, is not immediately decolorized by benzene. When

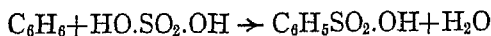
an alkaline permanganate solution is treated with the double-bond compound ethylene, it is decolorized immediately. There is, therefore, a difference between the behavior of benzene and a double-bond compound such as ethylene. When a solution of bromine dissolved in carbon tetrachloride is treated with the unsaturated, double-bond compound amylene it is decolorized immediately, but when treated with benzene it is not decolorized immediately. Benzene therefore does not unite readily by addition with certain reagents such as bromine, and consequently its behavior is different from that of the unsaturated compounds.

When halogens, such as chlorine or bromine, are allowed to act upon benzene in direct sunlight, addition products are formed, but much less readily than with unsaturated hydrocarbons. These addition products, however, never contain more than six halogen atoms. With bromine, for instance, benzene forms in direct sunlight benzene hexabromide,  $C_6H_6Br_6$ , and to this substance no more bromine can be added. When benzene is treated with chlorine or bromine at ordinary room temperature and in the absence of direct sunlight, substitution products such as monobrom benzene,  $C_6H_5Br$ , are obtained. These substitution products are formed more readily in the presence of a halogen carrier, such as iron, which facilitates the bromination.

Benzene is acted upon by concentrated nitric and sulfuric acids, yielding substitution products, and in this respect differs from the paraffin hydrocarbons. When treated with nitric acid, nitrobenzene,  $C_6H_5NO_2$ , is obtained:



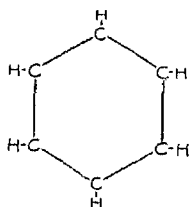
The interaction of benzene and sulfuric acid yields benzene sulfonic acid,  $C_6H_5SO_2.OH$ :



The various experimental facts which we have just mentioned show that the chemical behavior of benzene is quite different

from that of all the other hydrocarbons we have studied. Benzene is a very stable substance and in this respect resembles the saturated paraffins, but is quite unlike them in that it is readily acted upon by nitric and sulfuric acids. When treated with the halogens under different conditions, benzene forms both addition and substitution products, such as  $C_6H_6Br_6$  and  $C_6H_5Br$ . It is not easily oxidized when treated with vigorous oxidizing agents. Its behavior is therefore different from that of the unsaturated hydrocarbons.

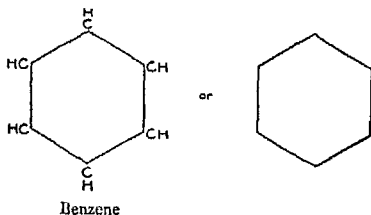
**Formula of benzene.** By studying the general chemical behavior of benzene and its derivatives, Kekulé in 1865 came to the conclusion that benzene could not be represented properly by a formula such as the open chains of the paraffins nor the



Benzene  
Figure 24

double bonds of the unsaturated hydrocarbons, because in certain respects benzene resembles and differs from both of these kinds of compounds in its chemical behavior. He therefore decided that the molecule of benzene is symmetrical and the six carbon atoms form a closed chain, or ring, and furthermore that each carbon atom is united to one hydrogen atom, as represented by the formula shown in Figure 24.

As the ring, or hexagon, formula of Kekulé was found to represent in a satisfactory manner the behavior of benzene, it has been accepted generally and is commonly written in the manner shown in Figure 25:



Benzene

Figure 25



Various arguments may be advanced to show that the ring formula of benzene agrees in a satisfactory manner with the chemical behavior of this substance. Benzene is a very stable compound, and the ring formula suggests stability. It is not easy experimentally to decompose benzene and "break the ring."

The formula shows that a molecule of benzene is symmetrical and all the hydrogen atoms have equal value or bear the same relation to the molecule. This is true because if we could make two compounds having the formula  $C_6H_5Br$ , but with different properties, we should conclude that all the hydrogen atoms in benzene do not bear the same relation to the molecule, and by substituting different hydrogen atoms by bromine we could obtain different monobrom derivatives. We cannot, however, prepare isomeric monosubstitution products of benzene. That is, we cannot prepare two monosubstitution products such as monobrom benzene,  $C_6H_5Br$ , having the same molecular formula but different properties, and therefore we conclude that all the hydrogen atoms bear the same relation to the molecule. A large number of experiments which were carried out to test this point showed that we can replace each hydrogen atom in benzene by a certain group such as the amino group and the same product, amino benzene,  $C_6H_5NH_2$ , is obtained in each case. Benzene is therefore represented by a symmetrical formula.

A consideration of the disubstitution products which benzene yields gives us convincing evidence of the symmetrical structure of the benzene molecule. When two hydrogen atoms in benzene are replaced by two univalent atoms or groups, three, and only three, isomeric disubstitution products are obtained. Thus we can prepare in the laboratory only three isomeric dibrom benzenes,  $C_6H_4Br_2$ , or three dimethyl benzenes (xylenes),  $C_6H_4(CH_3)_2$ . The existence of three isomeric disubstitution products of benzene is easily explained in accordance with the symmetrical ring formula. Let us consider the formulas of the dibrom derivatives

of benzene and for convenience number the angles of the hexagon at which the hydrogen atoms are situated.

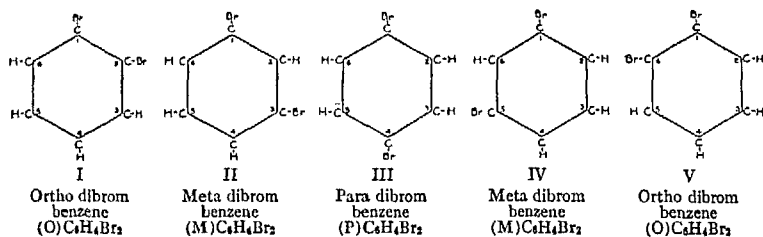


Figure 26

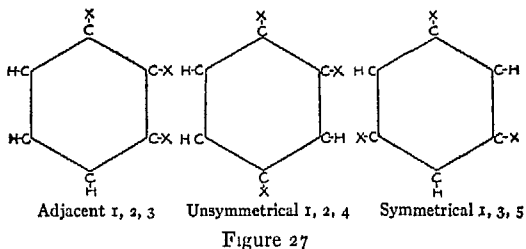
When two hydrogen atoms in benzene are substituted by two atoms of bromine, there are five possible arrangements by which this substitution may take place. As shown above, formulas I, II, and III are decidedly different. Formula IV is identical with II. This may not appear to be true, but if we were to lift up formula IV and turn it over, it would have the same appearance as formula II. In a like manner we may show that formula V is identical with formula I. Thus, although the dibrom benzenes may be represented by five different formulas, in reality only three of these formulas (I, II, and III) are distinctly different from each other. In each of these formulas the atoms are arranged differently in the molecule, and consequently each formula represents a different substance. The ring formula of benzene indicates, then, the existence of three different dibrom benzenes, and, as we have previously stated, only three dibrom benzenes can be prepared experimentally from benzene. The disubstitution products of benzene have been studied extensively, but no one has succeeded in making more than three dichlor benzenes or more than three of any other disubstitution product of benzene.

We have, therefore, three distinct classes of disubstitution products of benzene, which are known as **ortho**, **meta**, and **para** compounds. In the ortho compounds the substituted atoms

occupy the 1, 2 position, as shown in formula I, or they could be situated in any other adjacent position, such as 2, 3, or 3, 4 or 1, 6. In the meta compounds the substituted groups occupy the 1, 3 position or any similar position, such as the 2, 4 or 1, 5 position. In the para compounds the substituted atoms occupy the 1, 4 position or any similar position, such as the 2, 5 or 3, 6.

As the complete structural formulas of the disubstitution derivatives of benzene, such as ortho dibrom benzene, occupy a great deal of space, it is more convenient to designate these compounds in a more abbreviated manner, and accordingly the terms ortho, meta, or para are employed or simply the letters (O), (M), or (P). For example, instead of writing the complete structural formula of ortho dibrom benzene, we may write simply (O) dibrom benzene, and in a like manner (P) dichlor benzene would be an abbreviated expression for the complete structural formula of para dichlor benzene.

When three hydrogen atoms in benzene are substituted by three identical atoms, three isomeric trisubstitution products are obtained, as represented by the following general formulas, where X represents any substituted atom or group:



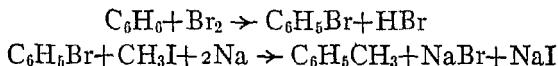
When four hydrogen atoms are substituted by identical atoms, three isomeric tetrasubstitution products of benzene are possible. With five hydrogen atoms replaced by identical atoms, only one derivative is possible, and likewise we can have only one hexasubstitution product.

When three or more hydrogen atoms are replaced by different

atoms or groups instead of identical atoms, a much larger number of isomeric derivatives is obtained.

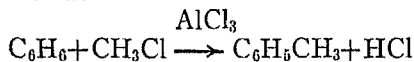
A ring formula, therefore, indicates the isomeric derivatives which benzene yields. As a large number of these derivatives has been prepared in the laboratory, this hypothesis of the benzene ring is in accordance with facts which have been established by experiment. Although the ring formula represents in a satisfactory manner the behavior of benzene, the formula itself is not entirely satisfactory because it represents each carbon atom as having a valence of only three. The fourth valence is not taken into consideration. This point has been discussed considerably in chemical literature and is still an unsettled question. Generally speaking, however, this is a matter of no special importance, because in most of the reactions of aromatic compounds the fourth bond remains undisturbed and need not be considered. Other formulas which represent each carbon atom as having four valences have been suggested, but objections have been raised to all of these formulas.

**Toluene**, (toluol)  $C_6H_5CH_3$ , is the second member of the benzene series of aromatic hydrocarbons. It may be obtained from coal tar and also by the dry distillation of balsam of Tolu, from which it derives its name. It may be prepared from benzene by first converting the benzene into brom benzene,  $C_6H_5Br$ , which is then treated with methyl iodide and sodium:

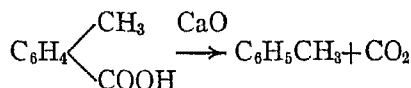


This method of preparing an aromatic hydrocarbon by treating an aromatic halogen compound with an aliphatic halogen compound and sodium is known as the *Fittig synthesis* and may be used for the preparation of other aromatic hydrocarbons. This synthesis is simply an application of the Wurtz reaction, which is used to prepare aliphatic hydrocarbons (see Ethane, page 27). Toluene may be prepared also by the synthesis of Friedel and

Craft, which consists in treating an aliphatic halogen compound with an aromatic hydrocarbon in the presence of anhydrous aluminium chloride:

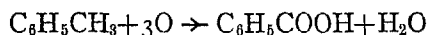


Toluene may be prepared also by heating toluic acid with soda lime:



This reaction is similar to that used in preparing benzene and is the general reaction which takes place when organic acids are heated with soda lime. The reactions used for the preparation of toluene are general reactions, which may be used to prepare other aromatic hydrocarbons.

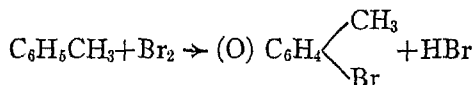
Toluene is a colorless liquid, boiling at  $110^\circ$ . It has a specific gravity of 0.8824 at  $0^\circ$  and a somewhat pleasant aromatic odor. In most respects it resembles benzene very closely, though it differs somewhat in chemical behavior, due to the presence of the methyl group. Toluene reacts with various substances, yielding a variety of substitution products. When treated with oxidizing agents, such as chromic acid or potassium permanganate, under the proper conditions, the methyl group is oxidized to the carboxyl group, while the phenyl group ( $\text{C}_6\text{H}_5$ ) is not acted upon:



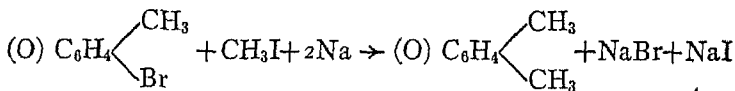
Judging from the methods which may be used to prepare toluene, it is monomethyl benzene. That is, it may be regarded as benzene in which one hydrogen atom has been replaced by the methyl group. Since the  $\text{C}_6\text{H}_5$  group is called the *phenyl radical*, toluene may be considered the phenyl derivative of methane and accordingly is called *phenyl methane*. It consists, therefore, of an aromatic radical united to an aliphatic radical.

Only one toluene has ever been prepared. What does this indicate?

**Xylenes**, (xylols)  $C_6H_4(CH_3)_2$ . The third member of the benzene series of aromatic hydrocarbons has two isomers; that is, there are three xylenes having the molecular formula  $C_8H_{10}$ . These xylenes are dimethyl derivatives of benzene. In our discussion of the benzene formula it was explained that only three isomeric disubstitution products of benzene are possible. We would, therefore, expect to have three dimethyl derivatives of benzene, and in reality only three xylenes have ever been discovered. These three xylenes occur in coal tar, from which they may be separated by fractional distillation. They cannot be separated from each other by distillation, since they have approximately the same boiling points; however, they can be separated by methods depending upon their differences in chemical behavior. These xylenes may be obtained from toluene. By the interaction of toluene and bromine at the ordinary room temperature, ortho and para brom toluenes are obtained:

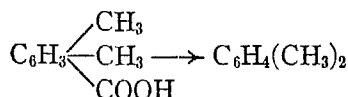


When ortho, or para, brom toluene is treated with methyl iodide and sodium, the corresponding ortho, or para, xylene is obtained:



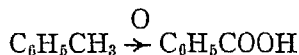
Meta brom toluene cannot be prepared directly from toluene. It may be prepared by other methods, which will be explained later. Meta xylene is obtained by the interaction of meta brom toluene, methyl iodide, and sodium. The three xylenes known as ortho, meta, and para may be obtained, then, from the corresponding brom toluenes. Meta xylene is more easily pre-

pared in pure condition by distilling mesitylenic acid,  $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{COOH}$ , with soda lime:



**Ortho xylene** boils at  $142^\circ$ , **meta xylene** boils at  $139^\circ$ , and **para xylene** has a boiling point at  $138^\circ$ . These three xylenes are inflammable liquids which have a rather pleasant odor. They resemble benzene and toluene in their general properties.

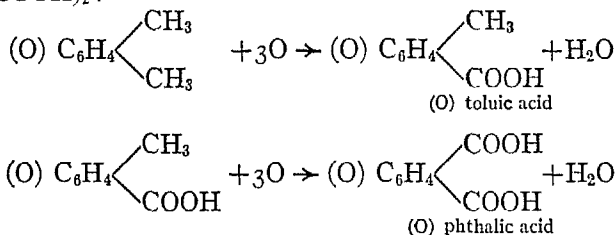
As previously stated, when toluene is oxidized the methyl group is converted into carboxyl:



The xylenes behave in a similar manner when oxidized and are converted into aromatic monobasic acids known as the *toluic acids*,

$\text{C}_6\text{H}_4 \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{COOH} \end{array}$ , which on further oxidation are converted

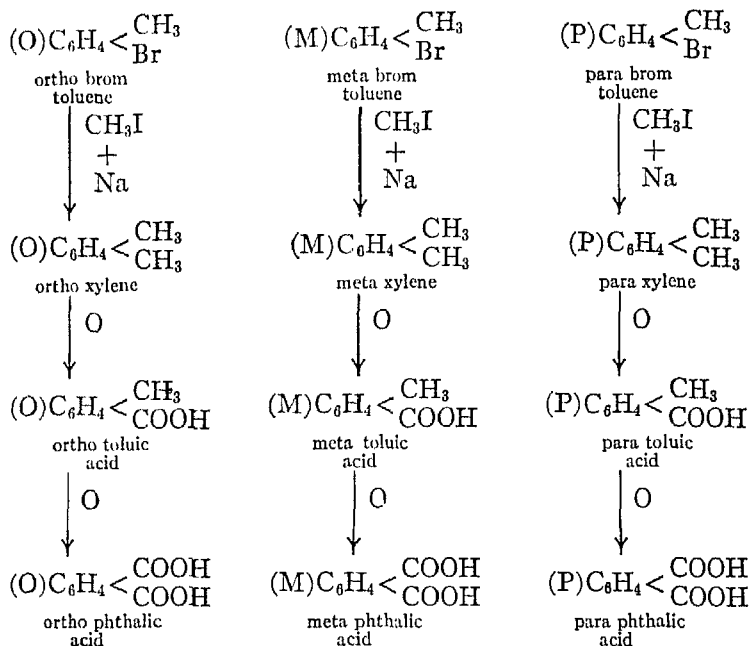
into aromatic dibasic acids known as the *phthalic acids*,  $\text{C}_6\text{H}_4(\text{COOH})_2$ :



Thus the three xylenes, ortho, meta, and para, yield three toluic acids which may be converted into the corresponding phthalic acids.

Observe that in the chemical changes which we have just described an ortho compound is converted into an ortho compound; a para compound yields a para compound; and a meta

compound gives a meta compound. This behavior of disubstitution products is again illustrated by the following outline equations:

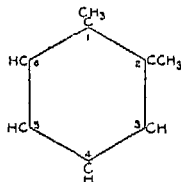
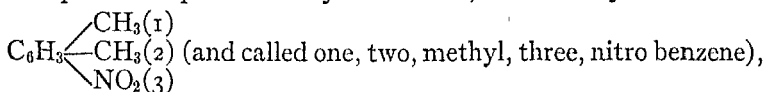


### Körner's method of distinguishing disubstitution products.

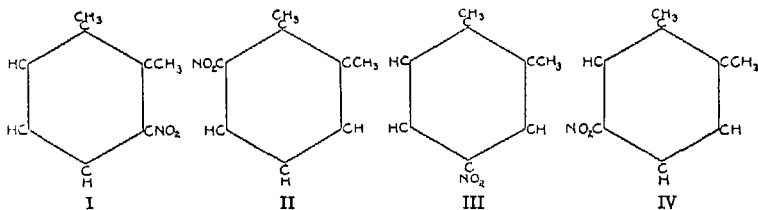
Suppose we had samples of the three xylenes and our bottles containing these samples were not labeled. How could we determine which of these samples was the ortho, meta, or para compound? Körner's method of solving this problem is based upon the fact that each disubstitution product of benzene, such as the xylenes, yields a different number of monosubstitution derivatives, such as monochlor or mononitro derivatives. As shown by the following formulas (Figs. 28 and 29), ortho xylene contains four hydrogen atoms [H(3), H(4), H(5), H(6)] which may be replaced by a nitro group.



Compounds represented by formula I, which may be written



Ortho xylene



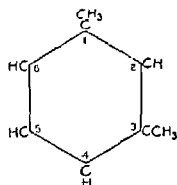
Figures 28 and 29

and by formula II,  $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3(1) \\ \text{CH}_3(2) \\ \text{NO}_2(6) \end{cases}$ , are identical, because in ortho

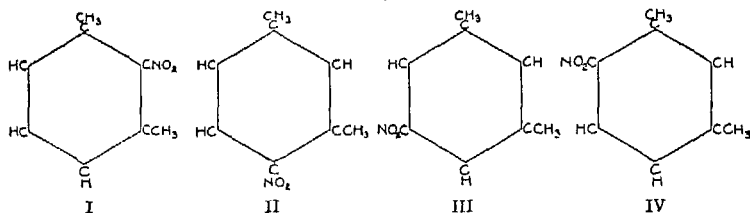
xylene the hydrogen atoms H(3) and H(6) adjacent to the methyl groups occupy similar positions in the molecule. Compounds represented by the formulas III and IV are identical, because in ortho xylene the hydrogen atoms H(4) and H(5), which are further removed from the methyl groups, also occupy similar positions in the molecule. Ortho xylene yields, then, two different nitro derivatives.

In meta xylene there are also four hydrogens, which may be replaced by nitro groups, as shown by the formulas given in Figures 30 and 31. Compounds represented by the formulas I, II, and III are distinctly different, while the substance represented by formula IV is identical with formula II. Meta xylene yields, then, three different nitro derivatives.

In para xylene the four hydrogen atoms are situated in a similar manner in the molecule, so that no matter which

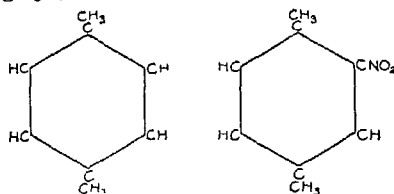


Meta xylene



Figures 30 and 31

hydrogen atom is replaced by a nitro group the same product is obtained (Fig. 32).



Para xylene

Figure 32

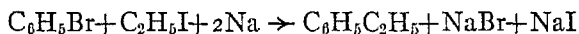
Para xylene yields, therefore, only one nitro derivative.

If we had, then, samples of the three xylenes, we could determine which was ortho, meta, or para by making nitro derivatives of these compounds. The ortho xylene would yield two isomeric nitro derivatives, meta xylene would give three nitro derivatives, and para one.

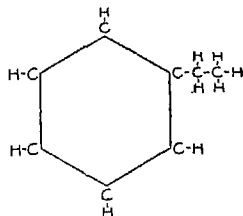
Results of numerous laboratory experiments have shown that what is true of the xylenes is true also of other disubstitution

products of benzene. Körner's method of distinguishing disubstitution products of benzene consists, then, in determining the number of isomeric monosubstitution products which each will yield. An ortho compound yields two isomeric monosubstitution derivatives, a meta compound yields three, and a para compound yields one.

**Ring and side chain.** As previously explained, there are various methods, such as the Fittig synthesis, which enable us to introduce a methyl group into benzene in place of one hydrogen atom. Just as we can introduce a methyl group into benzene, in a similar manner we can introduce other groups, such as ethyl or propyl, as is shown by the following reaction:



The substance having the formula  $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$  consists of an ethyl radical united to a phenyl radical and is called *ethyl benzene* or *phenyl ethane*. The complete structural formula of this substance would be that shown in Figure 33. It therefore consists of the benzene ring united to a side chain of carbon atoms. **Ethyl benzene** is a liquid which occurs in coal tar and boils at  $136^\circ$ . It is isomeric with the three xylenes, but may be distinguished from them by its action toward oxidizing



Ethyl benzene

Figure 33

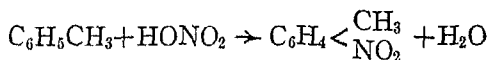
agents. When boiled with dilute nitric or chromic acids, it is converted into benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , which contains



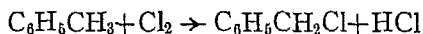
one carboxyl group,  $\text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{COOH}$ . The xylenes yield when oxidized the toluic acids,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{COOH} \\ \text{CH}_3 \end{smallmatrix}$ , which on further oxidation are converted into the phthalic acids,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{COOH} \\ \text{COOH} \end{smallmatrix}$ , containing two carboxyl groups. Ethyl benzene, therefore, resembles toluene and the xylenes in its behavior

toward oxidizing agents. When either of these substances undergoes oxidation, the aliphatic radical is converted into the carboxyl group. Experiments have shown that when a compound containing a ring and side chain is oxidized, the side chain, which may be a methyl, ethyl, propyl, or any other aliphatic radical, is always converted into the carboxyl group.

As we should naturally expect, a compound consisting of a ring united to an aliphatic side chain shows to a certain extent the behavior of both aromatic and aliphatic compounds, because the behavior of a compound is influenced by the groups it contains. For example, toluene,  $C_6H_5CH_3$ , consists of the benzene ring united to the methyl side chain. By the interaction of toluene and nitric acid, we obtain the compound nitro toluene,  $C_6H_4 < \begin{smallmatrix} CH_3 \\ NO_2 \end{smallmatrix}$ :



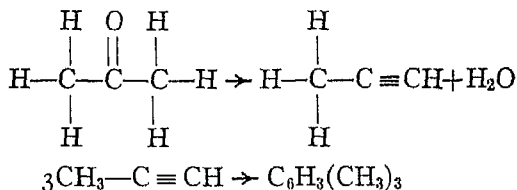
This is a reaction characteristic of aromatic compounds. When toluene is treated with chlorine under the proper conditions, the compound benzyl chloride,  $C_6H_5CH_2Cl$ , is obtained:



This reaction is characteristic of aliphatic compounds and is similar to that which takes place when methane is treated with chlorine. Again, the compound benzyl chloride when hydrolyzed behaves like methyl chloride; that is, the chlorine is replaced by hydroxyl, forming benzyl alcohol,  $C_6H_5CH_2OH$ :



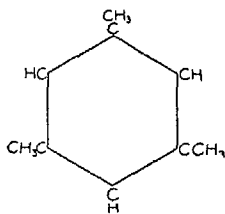
**Mesitylene**,  $C_6H_3(CH_3)_3$ , is the third member of the series of benzene hydrocarbons. It occurs in coal tar and is produced by distilling acetone in the presence of concentrated sulfuric acid:



The reaction really consists in the removal of water from acetone. The residues thus obtained from three molecules of acetone unite to form mesitylene. This synthesis indicates that mesitylene has a symmetrical formula as shown in Figure 34. Numerous experiments which have been performed have proved that mesitylene is represented correctly by a symmetrical formula.

Mesitylene is a colorless liquid which has a rather pleasant odor. It boils at  $164^\circ$  and distils with steam. When boiled with nitric acid, the methyl groups are converted into carboxyl.

The higher members of the benzene series generally behave in a manner similar to that of the lower members.



Mesitylene  
Figure 34

### GENERAL CHARACTERISTICS OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons like the aliphatic hydrocarbons may be grouped into homologous series, the simplest of which is the benzene series. In the table on page 298 are given a few of the simpler members of this series, with their isomers.

The lower members of the benzene series are colorless liquids which distil without decomposition and burn with a smoky flame. They are insoluble in water but dissolve in other solvents, such as ether and absolute alcohol. They dissolve fats, and other substances insoluble in water. Benzene, the first member of this series, is the fundamental substance from which the other aromatic hydrocarbons may be derived. The chemical behavior of benzene shows that it resembles to a certain extent

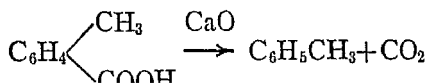
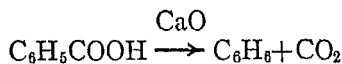
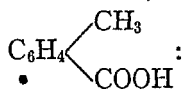
## ISOMERIC HYDROCARBONS OF THE BENZENE SERIES

MOLECULAR FORMULA	NAME		ABBREVIATED STRUCTURAL FORMULA	BOILING POINT °C.
C <sub>6</sub> H <sub>6</sub>	Benzene		C <sub>6</sub> H <sub>6</sub>	80.4
C <sub>7</sub> H <sub>8</sub>	Toluene		C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	110
C <sub>8</sub> H <sub>10</sub>	Dimethyl benzenes	(O) Xylene	(O)C <sub>6</sub> H <sub>4</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{CH}_3 \text{ (2)} \end{cases}$	142
		(M) Xylene	(M)C <sub>6</sub> H <sub>4</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{CH}_3 \text{ (3)} \end{cases}$	139
		(P) Xylene	(P)C <sub>6</sub> H <sub>4</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{CH}_3 \text{ (4)} \end{cases}$	138
	Ethyl benzene		C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	136
	C <sub>9</sub> H <sub>12</sub>	Trimethyl benzenes	Mesitylene	C <sub>6</sub> H <sub>3</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{CH}_3 \text{ (3)} \\ \text{CH}_3 \text{ (5)} \end{cases}$
Hemellithene			C <sub>6</sub> H <sub>3</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{CH}_3 \text{ (2)} \\ \text{CH}_3 \text{ (3)} \end{cases}$	175
Pseudo-cumene			C <sub>6</sub> H <sub>3</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{CH}_3 \text{ (2)} \\ \text{CH}_3 \text{ (4)} \end{cases}$	170
Normal propyl benzene		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	158.5	
Isopropyl benzene		C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	153	
Methyl ethyl benzenes			(O)C <sub>6</sub> H <sub>4</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{C}_2\text{H}_5 \text{ (2)} \end{cases}$	159
			(M)C <sub>6</sub> H <sub>4</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{C}_2\text{H}_5 \text{ (3)} \end{cases}$	159
			(P)C <sub>6</sub> H <sub>4</sub> $\begin{cases} \text{CH}_3 \text{ (1)} \\ \text{C}_2\text{H}_5 \text{ (4)} \end{cases}$	162

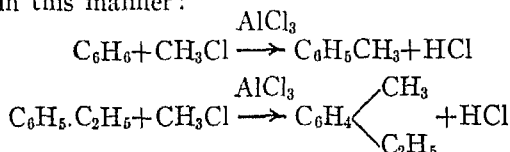
both single and double bond compounds and is best represented by a ring, or hexagon, formula. This formula shows that the molecule of benzene is symmetrical and that all the hydrogen atoms have equal value, and indicates the number of isomeric substitution products which benzene should yield. For instance, there should be no isomeric monosubstitution products; that is, there should be no compounds isomeric with methyl benzene. The fact is that only one toluene has ever been discovered. The hexagon formula indicates the existence of three isomeric disubstitution products, such as the three dimethyl benzenes (xylenes) and the three methyl ethyl benzenes. It is interesting to note that not more than three xylenes or three methyl ethyl benzenes have ever been discovered. This fact tends to confirm our view that the hexagon formula represents in a satisfactory manner the behavior of benzene. There are eight hydrocarbons having the molecular formula  $C_9H_{12}$ , as shown in the table above. The isomerism of the trimethyl benzenes and methyl ethyl benzenes is due to the fact that the substituted groups occupy different relative positions in the benzene ring. In the case of normal and isopropyl benzenes which are monosubstitution derivatives, the isomerism is due to the substituted groups and not to their position in the ring.

**Preparation.** Many of the aromatic hydrocarbons occur naturally in coal tar. They may be prepared synthetically by the general methods used to prepare aromatic hydrocarbons.

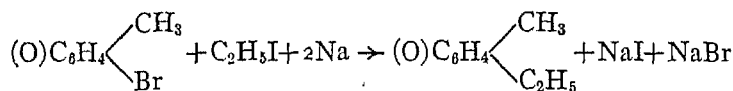
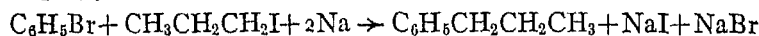
1. **Heating aromatic acids with lime or soda lime.** This is illustrated in the preparation of benzene from benzoic acid,  $C_6H_5COOH$ , and toluene from one of the toluic acids,



2. **Friedel and Crafts' reaction.** This synthesis consists in treating aromatic hydrocarbons with alkyl halogen compounds in the presence of anhydrous aluminium chloride. Thus, toluene, methyl ethyl benzene, and other aromatic hydrocarbons may be prepared in this manner:

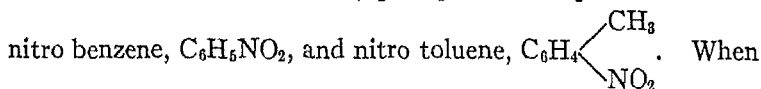


3. **Fittig's reaction.** In this method a halogen derivative of an aromatic hydrocarbon is treated with a halogen derivative of an aliphatic hydrocarbon in the presence of sodium. This is illustrated by the following reactions, showing the preparation of propyl benzene and methyl ethyl benzene:

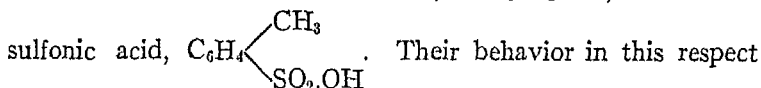


This method has an advantage over the other methods in that it shows the structure of the product obtained. Thus ortho brom toluene yields ortho methyl ethyl benzene. If meta, or para, brom toluene were used, the product of the reaction would be, of course, the corresponding meta, or para, methyl ethyl benzene.

**Chemical behavior.** Aromatic hydrocarbons resemble benzene and toluene in their general behavior. They react readily with concentrated nitric acid, giving nitro compounds such as



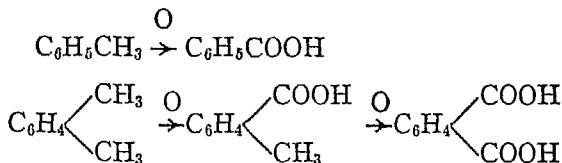
When treated with concentrated sulfuric acid, they yield sulfonic acids such as benzene sulfonic acid,  $\text{C}_6\text{H}_5\text{SO}_2\cdot\text{OH}$ , and toluene



Their behavior in this respect

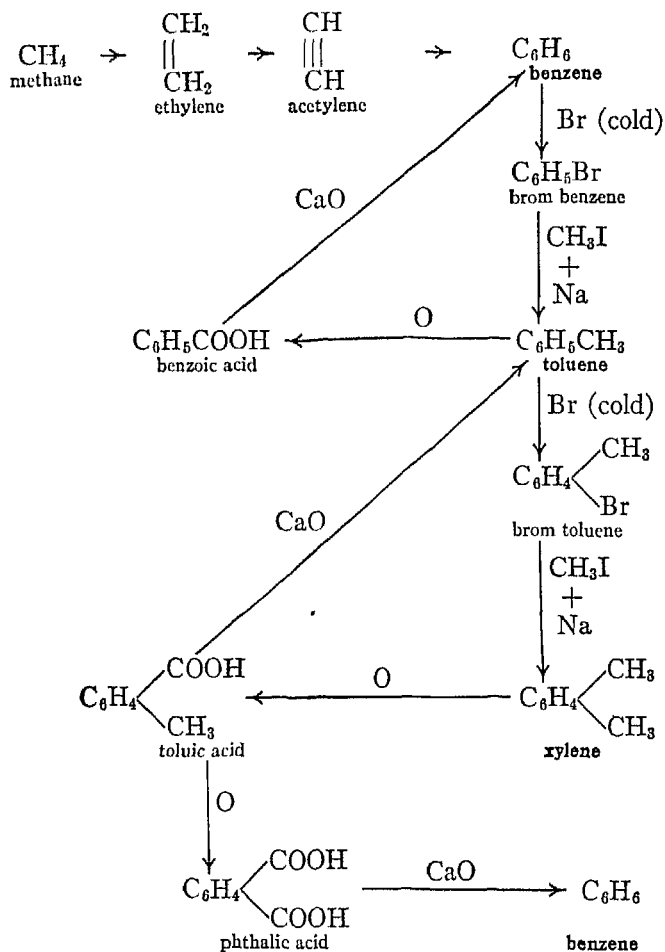


distinguishes them from the aliphatic hydrocarbons. They are very stable substances and are not easily decomposed, yielding compounds containing a smaller number of carbon atoms. However, when hydrocarbons such as toluene and the xylenes, which consist of the ring united to side chains, are treated with strong oxidizing agents, the side chains are slowly oxidized and converted into carboxyl groups:



The outline reactions on the following page show the synthetic relations between a few of the aliphatic hydrocarbons and the lower members of the benzene series.

## AROMATIC HYDROCARBONS



## QUESTIONS

1. What is the principal source of the aromatic hydrocarbons?
2. How is coal tar obtained?
3. How is illuminating gas obtained?
4. Explain, with equations, three general methods which are used for the preparation of aromatic hydrocarbons.
5. Write the following outline reactions:



6. Explain in accordance with the following questions how the hexagon formula represents the behavior of benzene:
  - a. Does benzene give reactions similar to both single- and double-bond compounds?
  - b. Do all the hydrogen atoms in benzene have equal value?
  - c. How many isomeric dimethyl derivatives does benzene yield?
7. From what two hydrocarbons is toluene derived? How does it behave when oxidized?
8. What happens to the methyl groups when ortho xylene is oxidized?
9. Which monobrom toluene yields ortho xylene?
10. What is Korner's method of distinguishing disubstitution products?
11. How is ethyl benzene prepared?
12. What is meant by the ring and side chain?
13. Write the complete structural formulas of benzene, toluene, ortho xylene, methyl ethyl benzene, and propyl benzene.
14. Write equations showing the preparation of methyl ethyl benzene and propyl benzene.
15. A compound has the empirical formula  $\text{C}_4\text{H}_4\text{O}$ . When distilled with lime it gave an aromatic liquid which when oxidized was converted to an acid having the molecular formula  $\text{C}_7\text{H}_6\text{O}_2$ . Write the formulas of these three compounds and the equations indicated.

## CHAPTER EIGHTEEN

### HALOGEN DERIVATIVES OF AROMATIC HYDROCARBONS

WE have considered briefly the simpler members of the benzene series of aromatic hydrocarbons. We are now going to study the halogen derivatives of these hydrocarbons.

When benzene is treated with chlorine or bromine in direct sunlight, addition products such as benzene hexachloride,  $C_6H_6Cl_6$ , are obtained. These addition products are not very stable. **Benzene hexachloride** is a crystalline substance which melts at  $157^\circ$ . When heated somewhat above its melting point, it is decomposed into hydrogen chloride and trichlor benzene,  $C_6H_3Cl_3$ :



When chlorine or bromine is allowed to act upon benzene at ordinary temperature and in the absence of direct sunlight, substitution products such as chlor benzene,  $C_6H_5Cl$ , and brom benzene,  $C_6H_5Br$ , are slowly formed. If the action is continued a sufficient length of time, all the hydrogen atoms in benzene are replaced by halogen, giving as final products hexachlor benzene,  $C_6Cl_6$ , or hexabrom benzene,  $C_6Br_6$ . The formation of these halogen substitution products is hastened considerably by the presence of a halogen carrier — that is, a substance such as iodine or iron which has the ability to accelerate the action.

**Chlor benzene**, (phenyl chloride)  $C_6H_5Cl$ , is a colorless liquid which has a rather pleasant odor. It boils at  $132^\circ$  and distils with steam. It may be prepared by the interaction of benzene and chlorine or by the application of the diazo reaction which will be described later.

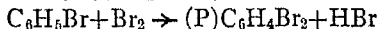
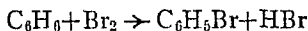
Benzene is not acted upon by iodine, but iodine substitution products of benzene may be prepared by indirect methods. **Iodobenzene**,  $C_6H_5I$ , is a colorless liquid which boils at  $188^\circ$ . It is prepared conveniently from diazo compounds.

**Brom benzene**,  $C_6H_5Br$ , is a colorless liquid resembling chlor

benzene and may be prepared by methods similar to those used in preparing chlor benzene.

## EXPERIMENT 65

Preparation of brom benzene,  $C_6H_5Br$ , and para dibrom benzene,  $(P)C_6H_4Br_2$



*Materials* { 30 cc. benzene  
20 cc. bromine  
1 gram of coarse iron filings  
20 grams of potassium hydroxide in 150 cc. water  
Ice water

*Procedure.* Arrange an apparatus as shown in the figure. An air condenser *E*, about 1.75 cm. in diameter, is connected to the 500 cc. flask *A*. A cork stopper through which passes a dropping funnel *C* and a tube *F* connecting the condenser to the filtering flask *B* is placed in the top of the air condenser. The filtering flask *B* contains a solution of 20 grams of potassium hydroxide dissolved in 150 cc. of water and is connected to the calcium chloride tube *D*, which contains soda lime. The object of the potassium hydroxide solution is to absorb the vapors of bromine and hydrogen bromide generated during the experiment. The soda lime absorbs the vapors escaping from the flask *B*.

Disconnect flask *A*, and place in it 1 gram of coarse iron filings and 30 cc. of benzene. The apparatus is again adjusted, with special care to have all connections very firm and secure. Pour 20 cc. of bromine into the dropping funnel *C*. Open the stopcock of the drop-

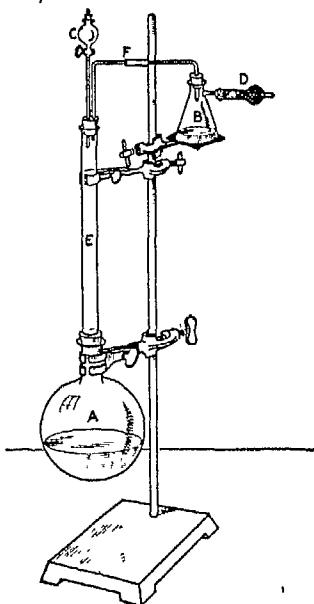


Figure 35

ping funnel *C*, and allow about 6 cc. of bromine to flow into flask *A*. If the first reaction becomes too vigorous, place a bath of ice water under flask *A*, and allow it to remain there a few minutes until the energetic action has subsided. If no action begins, allow about 4 cc. more of bromine to flow into flask *A*; if necessary, warm flask *A* slightly to start the action, but be prepared to cool it in case the action becomes too violent. Finally, when the first action has slowed down considerably, gradually add the rest of the bromine in portions of about 5 cc. When the main reaction is over, flask *A* is heated until no more bromine vapors are visible in the flask.

The apparatus is now disconnected, and the reaction product in flask *A* is poured into a beaker to separate it from the iron filings. The reaction product is now treated with a dilute potassium hydroxide solution (2 grams dissolved in 15 cc. of water), poured into a separating funnel, and the lower heavy layer separated. This lower layer is then washed with water, separated again, placed in a liter round flask, and steam distilled. The apparatus is arranged as shown in

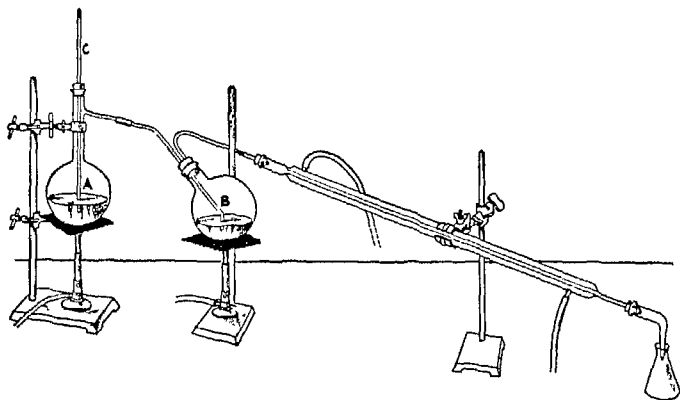


Figure 36

Figure 36. The reaction product which has been washed with the alkali solution and water is placed in flask *B*, and to it is added about 400 cc. of water. Flask *A* contains about 600 cc. of water and is fitted with a safety tube *C*. The reaction product is steam distilled by heating both flasks and passing steam from flask *A* into flask *B*.

When all the brom benzene has passed over, crystals of the para dibrom benzene begin to separate in the condenser. The receiver is

now changed, and by periodically removing the water in the condenser all the dibrom benzene can be distilled over.

The first distillate is poured into a separating funnel and the lower heavy layer of liquid monobrom benzene separated, and poured into an Erlenmeyer flask. To it are added a few small pieces of dry, granular calcium chloride, and the flask is tightly stoppered. When the oil is dehydrated and does not present a milky appearance, it is filtered and distilled. Collect the fraction boiling between  $150^{\circ}$  to  $160^{\circ}$ . Monobrom benzene boils at  $155^{\circ}$ .

The second distillate containing the solid dibrom benzene is filtered. The colorless crystals of (P) dibrom benzene are dried on filter paper and recrystallized from hot alcohol. Melting point  $89^{\circ}$ . Preserve specimens of brom benzene and para dibrom benzene, and calculate the yields.

The monohalogen derivatives of benzene are colorless liquids and very stable substances. Brom benzene, for example, is not hydrolyzed by water, and is not acted upon by alkalies, or silver acetate. In this respect it differs from ethyl bromide (Experiment 17). As a rule a halogen atom which is united to the carbon of the benzene ring is held very firmly and is not easily removed.

Most of the dihalogen substitution products of benzene, such as para dibrom benzene, are crystalline solids which are insoluble in water but soluble in alcohol and ether.

In the table on pages 308 and 309 are given the chlorine derivatives of benzene and a few of the chlorine derivatives of toluene.

In the discussion of the formula of benzene it was pointed out that when the hydrogen atoms in benzene are substituted by identical atoms such as chlorine we obtain one monosubstitution product such as chlor benzene. When two hydrogen atoms are substituted by chlorine, we obtain three isomeric disubstitution products, which are the ortho, meta, and para compounds. Three hydrogen atoms substituted by chlorine yield three isomeric trichlor benzenes, which are the symmetrical, adjacent, and unsymmetrical derivatives. These terms, of course, refer to the positions occupied by the chlorine. Four hydrogen atoms sub-

## CHLORINE DERIVATIVES OF BENZENE AND TOLUENE

NAME		FORMULA	MELTING POINT, °C	BOILING POINT, °C.
Benzene hexachloride		$C_6H_6Cl_6$	157	
Monochlor benzene		$C_6H_5Cl$		132
Dichlor benzenes	Ortho	$(O)C_6H_4 \begin{matrix} \swarrow Cl & (1) \\ \searrow Cl & (2) \end{matrix}$		179
	Meta	$(M)C_6H_4 \begin{matrix} \swarrow Cl & (1) \\ \searrow Cl & (3) \end{matrix}$		172
	Para	$(P)C_6H_4 \begin{matrix} \swarrow Cl & (1) \\ \searrow Cl & (4) \end{matrix}$	53	173
Trichlor benzenes	Symmetrical	$C_6H_3 \begin{matrix} \swarrow Cl & (1) \\ \swarrow Cl & (3) \\ \searrow Cl & (5) \end{matrix}$	54	208
	Adjacent	$C_6H_3 \begin{matrix} \swarrow Cl & (1) \\ \swarrow Cl & (2) \\ \searrow Cl & (3) \end{matrix}$	16	218
	Unsymmetrical	$C_6H_3 \begin{matrix} \swarrow Cl & (1) \\ \swarrow Cl & (2) \\ \searrow Cl & (4) \end{matrix}$	63	213
Tetrachlor benzenes	Symmetrical	$C_6H_2 \begin{matrix} \swarrow Cl & (1) \\ \swarrow Cl & (2) \\ \swarrow Cl & (4) \\ \searrow Cl & (5) \end{matrix}$	137	244
	Adjacent	$C_6H_2 \begin{matrix} \swarrow Cl & (1) \\ \swarrow Cl & (2) \\ \swarrow Cl & (3) \\ \searrow Cl & (4) \end{matrix}$	46	254
	Unsymmetrical	$C_6H_2 \begin{matrix} \swarrow Cl & (1) \\ \swarrow Cl & (2) \\ \swarrow Cl & (3) \\ \searrow Cl & (5) \end{matrix}$	50	246



\* CHLORINE DERIVATIVES OF BENZENE AND TOLUENE (*continued*)

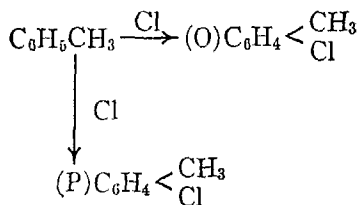
NAME		FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Pentachlor benzene		$C_6HCl_5$	86	276
Hexachlor benzene		$C_6Cl_6$	226	326
Chlor toluenes	Ortho	$(O)C_6H_4 \begin{matrix} \diagup CH_3 (1) \\ \diagdown Cl (2) \end{matrix}$		154
	Meta	$(M)C_6H_4 \begin{matrix} \diagup CH_3 (1) \\ \diagdown Cl (3) \end{matrix}$		150
	Para	$(P)C_6H_4 \begin{matrix} \diagup CH_3 (1) \\ \diagdown Cl (4) \end{matrix}$		160
Benzyl chloride		$C_6H_5CH_2Cl$		176

stituted by chlorine yield three isomeric derivatives, which are the symmetrical, adjacent, and unsymmetrical. There is only one pentachlor benzene and one hexachlor benzene. These facts are well illustrated in the preceding table. The various tri- and tetrachlor benzenes as well as pentachlor and hexachlor benzene may be prepared by suitable methods, but it would lead too far into the subject at present to discuss the exact methods which may be used to prepare these compounds.

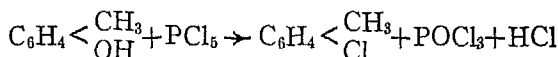
**Halogen derivatives of toluene.** Toluene,  $C_6H_5CH_3$ , consists of a phenyl radical, or ring, united to a methyl side chain. Halogen substitution products of toluene may be obtained by substituting hydrogen atoms in the ring or in the side chain. Toluene therefore yields two classes of halogen substitution products, such as the chlor toluenes,  $C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown Cl \end{matrix}$ , and benzyl chloride,  $C_6H_5CH_2Cl$ .

**Chlor toluenes,**  $C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown Cl \end{matrix}$ . As chlor toluene is a disubstitution product of benzene, there are, of course, three isomeric

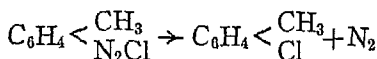
chlor toluenes (O, M, and P). When cold toluene is treated with chlorine in the presence of a halogen carrier, such as iodine or iron, substitution takes place in the ring and a mixture of ortho and para chlor toluenes is obtained :



The boiling point of ortho chlor toluene is  $154^\circ$ , and para chlor toluene boils at  $160^\circ$ . As the difference between the boiling points of the ortho and para chlor toluenes is very small, it is impossible to separate them by fractional distillation. These compounds, therefore, cannot be obtained easily in pure condition by the interaction of toluene and chlorine. They may be obtained separately by treating the corresponding cresols,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_3 \\ \text{OH} \end{array}$ , with phosphorous pentachloride (see Cresol reactions, pages 369-372) :

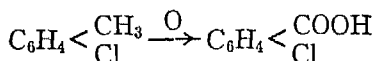


Meta chlor toluene may be prepared in like manner from meta cresol. It boils at  $150^\circ$ . The three chlor toluenes may be obtained also by the decomposition of diazo compounds (see Sandmeyer reaction, page 340) :

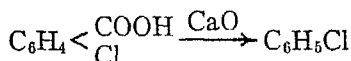


In certain respects the chemical behavior of the chlor toluenes resembles that of toluene. When toluene is oxidized, the methyl group is converted into carboxyl, yielding benzoic acid,

$C_6H_5COOH$ . In like manner the chlor toluenes when oxidized are converted into the corresponding chlor benzoic acids:



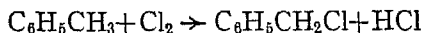
Notice that in the reaction above, the chlorine atom which is united to the ring is held firmly and is not removed when the compound is oxidized. When benzoic acid is distilled with lime it yields benzene, and in like manner chlor benzoic acid distilled with lime yields monochlor benzene:



Monohalogen derivatives of benzene may therefore be obtained in pure condition from the halogen-substituted benzoic acids.

The brom toluenes,  $C_6H_4<\begin{smallmatrix} CH_3 \\ Br \end{smallmatrix}$ , are prepared by reactions similar to those used in preparing the chlor toluenes. The iodo toluenes are obtained most conveniently by means of the Sandmeyer reaction.

When chlorine or bromine acts upon toluene in sunlight, or at a boiling temperature, substitution takes place in the side chain, and compounds such as benzyl chloride,  $C_6H_5CH_2Cl$ , are obtained:



By the continued action of chlorine or bromine upon boiling toluene the remaining hydrogen atoms in the side chain are replaced by halogen, yielding compounds such as benzal chloride,  $C_6H_5CHCl_2$ , and benzotrichloride,  $C_6H_5CCl_3$ .

**Benzyl chloride**,  $C_6H_5CH_2Cl$ , contains one halogen atom in the side chain and is isomeric with the three chlor toluenes,  $C_6H_4<\begin{smallmatrix} CH_3 \\ Cl \end{smallmatrix}$ , each of which has one halogen atom in the ring. It is prepared by passing chlorine into boiling toluene and may be

obtained also by the interaction of benzyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ , and phosphorous pentachloride:



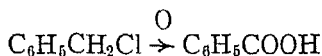
Benzyl chloride is a colorless liquid which boils at  $176^\circ$ . It has a very unpleasant, irritating odor and is soluble in alcohol and ether but insoluble in water. The chemical behavior of benzyl chloride distinguishes it from the isomeric chlor toluenes. In benzyl chloride the atom of chlorine is united to the side chain and is not held so firmly as the halogen atom in compounds such as brom benzene and the chlor toluenes, in which the halogen atom is united directly to the ring. When benzyl chloride is hydrolyzed, the chlorine is easily replaced by hydroxyl, forming benzyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ :



Benzyl chloride reacts with silver acetate, yielding benzyl acetate,



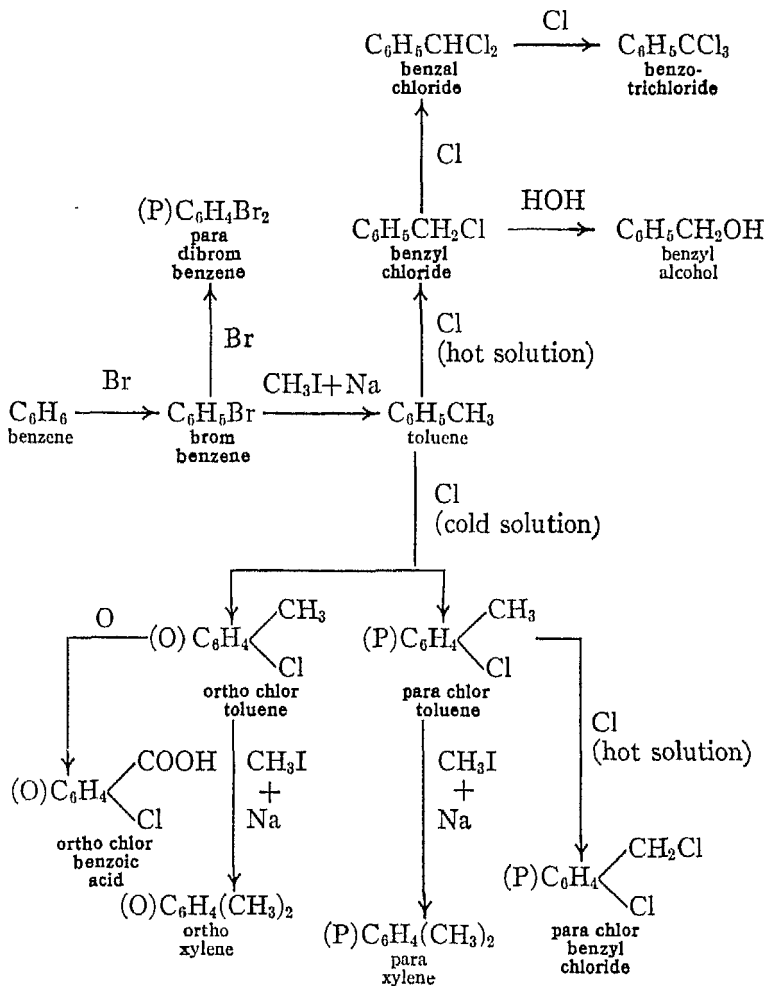
When benzyl chloride is oxidized with dilute nitric acid, it is converted into benzoic acid,



Since the chlorine atom is easily eliminated from the molecule of benzyl chloride, as shown by the reaction above, this fact shows that the chlorine atom in benzyl chloride is situated in the side chain and not in the ring. Benzyl chloride is prepared commercially for the manufacture of benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , and is therefore a substance of considerable commercial importance.

**Benzal chloride**,  $\text{C}_6\text{H}_5\text{CHCl}_2$ , is a colorless liquid which boils at  $206^\circ$ . It is used also in the manufacture of benzaldehyde. Benzotrichloride, or phenyl chloroform,  $\text{C}_6\text{H}_5\text{CCl}_3$ , boils at  $213^\circ$ . When hydrolyzed it is converted into benzoic acid. It is used in the manufacture of benzoic acid.

## AROMATIC HALOGEN COMPOUNDS



As we have just explained, we can introduce chlorine into the ring or side chain of toluene. By arranging properly the experimental condition, we can introduce chlorine into both the ring and side chain. This may be done in the following manner:

We could prepare first para chlor toluene  $(P)C_6H_4 < \begin{smallmatrix} CH_3 \\ Cl \end{smallmatrix}$ . By passing chlorine into a boiling solution of para chlor toluene, substitution takes place in the side chain, forming the compound para chlor benzyl chloride,  $(P)C_6H_4 < \begin{smallmatrix} CH_2Cl \\ Cl \end{smallmatrix}$ .

The outline reactions on the previous page show the synthetic relations between the lower members of the benzene series and their simple halogen derivatives.

### QUESTIONS

1. Explain, with equations, the laboratory preparation of brom benzene and para dibrom benzene.
2. Write structural formulas of the dichlor benzenes.
3. Write equations showing the introduction of chlorine into the ring and side chain of toluene.
4. What is formed by the oxidation of ortho chlor toluene?
5. What is formed by the hydrolysis of benzyl chloride?
6. What is obtained by the oxidation of benzyl chloride?
7. Write structural formulas of (O) chlor toluene, benzal chloride, trichlor benzene (1) (2) (3), and benzene hexachloride.
8. Write equations showing the preparation of (P) chlor benzyl chloride.
9. Write the following outline equations:
  - a. benzene  $\rightarrow$  toluene  $\rightarrow$  benzyl alcohol.
  - b. benzene  $\rightarrow$  toluene  $\rightarrow$  ortho xylene.
10. A compound on investigation was shown to have the molecular formula  $C_6H_4Br_2$ . How could you determine whether it was an ortho, meta, or para compound?

## CHAPTER NINETEEN

### NITRO COMPOUNDS

ALIPHATIC hydrocarbons such as methane and ethane do not react with nitric acid, however aliphatic nitro compounds may be prepared indirectly. When methyl iodide is treated with silver nitrite, the compound nitro methane,  $\text{CH}_3\text{NO}_2$ , which contains the nitro ( $\text{NO}_2$ ) group, is obtained :



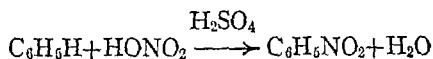
Nitro methane is a colorless liquid which boils at  $101^\circ$ . Although quite a number of nitro derivatives of the paraffin hydrocarbons have been prepared, they are not compounds of special importance.

The aromatic hydrocarbons react readily with concentrated nitric acid, forming nitro compounds in which one or more of the hydrogen atoms in the benzene ring have been substituted by nitro groups. These aromatic nitro compounds are very important substances because they are used for the preparation of other compounds of considerable importance. When benzene is treated with concentrated nitric acid, the compound nitro benzene,  $\text{C}_6\text{H}_5\text{NO}_2$ , is obtained :



The process of introducing nitro groups into an aromatic hydrocarbon is known as *nitration*. In nitrating aromatic hydrocarbons, the nitration is usually effected more readily by using a nitrating mixture consisting of concentrated nitric and sulfuric acids. In this nitrating process the sulfuric acid unites with the water formed in the reaction and thus prevents the dilution of the nitric acid.

## EXPERIMENT 66

Preparation of nitro benzene, (oil of mirbane)  $C_6H_5NO_2$ 

Materials { 60 cc. concentrated sulfuric acid  
52 cc. concentrated nitric acid  
42 cc. benzene

*Procedure.* Pour 60 cc. of concentrated sulfuric acid into a 500 cc. round flask. The flask is held under running tap water or immersed in a tank of cold water. Gradually add to the sulfuric acid, with constant shaking and cooling, 52 cc. of concentrated nitric acid. When this nitrating mixture has been prepared and cooled to room temperature, gradually add 42 cc. of benzene, with frequent shaking and cooling. The flask is now connected to an air condenser, and immersed in a water bath heated to about  $50^\circ$ . The temperature of this bath should not rise above  $50^\circ$ , as otherwise some dinitro benzene may be formed. The mixture should be shaken from time to time and allowed to remain at this temperature about 40 minutes, after which it is poured into a separating funnel and the top layer of oil separated from the acid solution. The oil is washed by adding about 70 cc. of water, shaking, and separating the lower heavy layer of oil from the upper aqueous solution. The oil is now washed with 70 cc. of a dilute solution of sodium carbonate (1:20), and again with 70 cc. of water. In each case the oil is the heavier layer and is withdrawn from the bottom of the separating funnel. It is now placed in an Erlenmeyer flask; add a few small pieces of granulated calcium chloride to dehydrate it. (See that the flask is firmly stoppered to prevent access of moisture.) When the yellow liquid is clear, showing that the dehydration is complete, filter into a 200 cc. distilling flask and distil through a condenser. Collect the fraction boiling between  $204^\circ$  and  $210^\circ$ . Nitro benzene boils at  $208^\circ$ . Preserve a specimen and calculate the yield.

Nitro benzene, or oil of mirbane, is a yellow oil having a strong odor like that of benzaldehyde,  $C_6H_5CHO$ , (oil of bitter almonds). It is insoluble in water but soluble in alcohol, ether, and benzene. It has a specific gravity of 1.2 at  $20^\circ$ , is poisonous, and distills with steam. It is manufactured commercially in



large quantities for use in the preparation of synthetic dyes. It is used also in the preparation of perfumery and as a solvent for organic compounds.

**Drying agents.** In the preparation of organic compounds the crude reaction product is usually contaminated by impurities. The impure product is frequently treated with various solutions, after which it is washed with water. In the case of liquids it is usually necessary to dry them before distilling. For instance, in the preparation of nitro benzene, the reaction product obtained by treating benzene with the nitrating solution is washed with water, sodium carbonate solution, and again with water. After each treatment the nitro benzene is separated carefully from the wash solution. The nitro benzene still contains a very small quantity of water which renders it turbid. This is removed by treating with the drying agent, calcium chloride. The drying agents most frequently employed are given below :

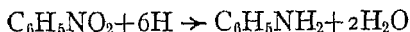
<i>Drying agents</i>	{	Calcium chloride (granulated)
		Potassium hydroxide
		Sodium sulfate (anhydrous)
		Calcium oxide
		Potassium carbonate (anhydrous)
		Copper sulfate (anhydrous)

In using drying agents it is necessary to select an appropriate substance which will not react with the compound to be dried. The substance usually employed is anhydrous, granular calcium chloride (see Experiments 11, 18, 28, 65, and 66). Since calcium chloride forms double compounds with alcohols and phenols, it cannot be used to dry these substances (Experiments 15, 75, 78).

Solid potassium hydroxide is used to remove water from basic substances such as aniline (Experiment 68). Potassium hydroxide reacts with acids and phenols, yielding salts. It also saponifies esters, and therefore cannot be used to dry these substances.

Anhydrous sodium sulfate is used to dry phenols (Experiments 75 and 78). Calcium oxide, potassium carbonate, and copper sulfate are also used as drying agents in special cases (Experiments 15 and 81).

**Characteristics of nitro compounds.** The nitro group in most of the aromatic nitro compounds is held very firmly and is not easily replaced by other atoms or groups. When nitro benzene is reduced with hydrogen, the nitro group is converted into the amino group, yielding amino benzene, or aniline,  $C_6H_5NH_2$ :

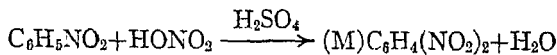


This is the most important reaction of nitro benzene. As other nitro compounds behave in a similar manner, this reduction reaction is the most important characteristic of nitro compounds. Since nitro compounds when reduced are converted into amines, this fact is considered sufficient evidence, indicating that in the nitro compounds the nitrogen atom is joined to the ring. The structural formula of nitro benzene is therefore  $C_6H_5-N \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ .

When benzene is treated with a larger quantity of a nitrating solution and at a somewhat elevated temperature, **meta dinitro benzene**,  $(M)C_6H_4(NO_2)_2$ , is obtained, together with small amounts of the ortho and para compounds. Meta dinitro benzene may be obtained also by nitrating nitro benzene.

#### EXPERIMENT 67

**Preparation of meta dinitro benzene,  $(M)C_6H_4(NO_2)_2$**

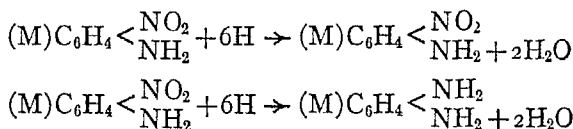


*Materials*  $\left\{ \begin{array}{l} 13 \text{ cc. nitro benzene} \\ 28 \text{ cc. concentrated nitric acid} \\ 30 \text{ cc. concentrated sulfuric acid} \end{array} \right.$

**Procedure.** The nitrating solution is prepared in a 200 cc. flask by adding slowly 28 cc. of concentrated nitric acid to 30 cc. concentrated sulfuric acid with constant shaking and cooling; 13 cc. of nitro benzene is now added slowly from a dropping funnel to the nitrating

solution. During the addition of the nitro benzene the flask should be shaken frequently, but it is not necessary to cool it. When the materials have been mixed, the flask containing the mixture is heated upon a boiling water bath under a hood for about 2 hours. To test if the nitration has been complete, pour a few drops of the mixture into about 50 cc. of ice water. If the nitration is complete, the dinitro benzene will separate as a yellow solid; if not, it separates as a semisolid, in which case the heating must be continued with the addition of a little more of the nitrating mixture. When the nitration is complete, cool, and pour the product into about 600 cc. of cold water. Filter, dry on filter paper, and recrystallize from hot ethyl alcohol. Melting point  $90^{\circ}$ . Preserve a specimen and calculate the yield.

Meta dinitro benzene crystallizes in pale-yellow needles. It distills with steam and is soluble in hot alcohol and various other organic solvents. When reduced with alcoholic ammonium sulfide, the nitro groups are converted into amino groups. The first product of the reduction is meta nitraniline,  $(M)C_6H_4 \begin{smallmatrix} N_2O \\ \diagdown \\ NH_2 \end{smallmatrix}$ , and this on further reduction is converted into meta diamino benzene, (meta phenylene diamine)  $(M)C_6H_4(NH_2)_2$ :



The ortho and para dinitro benzenes behave in a similar manner when reduced and also yield diamines,  $C_6H_4(NH_2)_2$ .

Symmetrical trinitro benzene,  $C_6H_3 \begin{smallmatrix} NO_2(1) \\ \diagdown \\ NO_2(3) \\ \diagup \\ NO_2(5) \end{smallmatrix}$ , is obtained by

the continued nitration of meta dinitro benzene. It is a crystalline substance which melts at  $121^{\circ}$ .

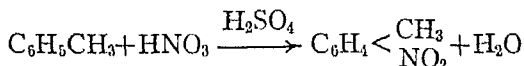
• When a compound is nitrated, the number of nitro groups which may be introduced into the compound in place of hydrogen atoms depends upon the strength of the nitrating mixture, temperature, and composition of the substance. Usually when nitrating with a more concentrated mixture of acids and at

higher temperatures more nitro groups are introduced into the compound. As we have already stated, it is comparatively easy to introduce one or two nitro groups into a compound. The introduction of three nitro groups is usually accomplished with difficulty. Attempts which have been made to introduce more than three nitro groups have generally proved unsuccessful. The nitro groups usually replace the hydrogen atoms in the ring and only very seldom enter the side chain. In the following table are given a few of the nitro derivatives of benzene and toluene :

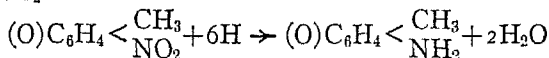
NITRO COMPOUNDS

NAME		FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Nitro benzene		$C_6H_5NO_2$	3	208
Dinitro benzenes	Ortho	$(O)C_6H_4 \begin{cases} NO_2 \text{ (1)} \\ NO_2 \text{ (2)} \end{cases}$	117	319
	Meta	$(M)C_6H_4 \begin{cases} NO_2 \text{ (1)} \\ NO_2 \text{ (3)} \end{cases}$	90	302
	Para	$(P)C_6H_4 \begin{cases} NO_2 \text{ (1)} \\ NO_2 \text{ (4)} \end{cases}$	172	299
Nitro toluenes	Ortho	$(O)C_6H_4 \begin{cases} CH_3 \text{ (1)} \\ NO_2 \text{ (2)} \end{cases}$	-10.5	218
	Meta	$(M)C_6H_4 \begin{cases} CH_3 \text{ (1)} \\ NO_2 \text{ (3)} \end{cases}$	16	230
	Para	$(P)C_6H_4 \begin{cases} CH_3 \text{ (1)} \\ NO_2 \text{ (4)} \end{cases}$	54	234
Phenyl nitro methane		$C_6H_5CH_2NO_2$		226 decomposes

**Nitro toluenes**,  $C_6H_4<\begin{smallmatrix} CH_3 \\ NO_2 \end{smallmatrix}$ . When toluene is nitrated, a mixture of ortho and para nitro toluenes is obtained, together with a very small amount of meta nitro toluene:



Ortho nitro toluene melts at  $-10.5^\circ$  and boils at  $218^\circ$ . Meta nitro toluene melts at  $16^\circ$  and boils at  $230^\circ$ . The melting point of para nitro toluene is  $54^\circ$  and the boiling point  $234^\circ$ . These substances have a yellow color and an odor somewhat like that of nitro benzene. They resemble nitro benzene in their general chemical behavior. They are substances of considerable importance, because when they are reduced they yield the toluidines,  $C_6H_4<\begin{smallmatrix} CH_3 \\ NH_2 \end{smallmatrix}$ , which are valuable technical compounds:



By the continued nitration of toluene, dinitro toluenes,  $C_6H_3CH_3(NO_2)_2$ , and trinitro toluenes,  $C_6H_2CH_3(NO_2)_3$ , are obtained. Trinitro toluene, T. N. T., is a yellowish crystalline powder which melts at about  $79^\circ$ . It explodes with great violence, giving a quantity of black smoke when detonated by mercuric fulminate. It is a very high-power explosive.

**Phenyl nitro methane**,  $C_6H_5CH_2NO_2$ , is obtained by heating toluene with dilute nitric acid for a considerable length of time:



It may be prepared also by the interaction of silver nitrite and benzyl iodide,  $C_6H_5CH_2I$ . In this substance we have the nitro group introduced into the side chain, which is quite unusual, because when aromatic hydrocarbons are nitrated the nitro group usually enters the ring. Phenyl nitro methane is a colorless oil. When heated at the temperature of its boiling point,  $226^\circ$ , it is decomposed.

## INFLUENCE OF SUBSTITUTED GROUPS

We began our study of aromatic compounds by considering the aromatic hydrocarbons. The aromatic hydrocarbons yield substitution products when treated with nitric and sulfuric acids and halogens, such as chlorine and bromine. The position taken by an atom or group entering an aromatic compound is determined by the directing influence of the atoms or groups which are already present. If a compound contains one of the following atoms or groups, Cl, Br, I,  $\text{NH}_2$ , OH, or one of the alkyl groups, and the entering group is one of the following, Br, Cl,  $\text{NO}_2$ ,  $\text{SO}_2\text{OH}$ , or alkyl, the reaction product will be a para compound which is usually accompanied by small amounts of ortho. Thus the bromination of benzene yields first brom benzene and then para dibrom benzene (see Experiment 65, page 305). The presence of the first bromine atom directs the second to the para position. Again, phenol,  $\text{C}_6\text{H}_5\text{OH}$ , when nitrated (see Experiment 77, page 366) yields the ortho and para nitro phenols. If a compound contains  $\text{NO}_2$ ,  $\text{COOH}$ ,  $\text{SO}_2\text{OH}$ ,  $\text{CHO}$ ,  $\text{CH}_3\text{CO}$ , or  $\text{CN}$ , and the entering group is one of those mentioned above, then the principal product is a meta compound which is usually accompanied by small amounts of ortho and para compounds. Thus, when benzene is nitrated, the first product is nitro benzene, which on further nitration yields meta dinitro benzene (Experiment 67, page 318).

## QUESTIONS

1. What is meant by nitration?
2. How are compounds usually nitrated?
3. Explain, with equations, the laboratory preparation of nitro benzene and meta dinitro benzene. How are these compounds purified?
4. What is the most important characteristic of nitro compounds?
5. When a compound is nitrated, do the nitro groups usually enter the ring or side chain?
6. Write the complete structural formulas of the following compounds; nitro benzene; meta dinitro benzene; ortho nitro toluene; phenyl nitro methane.
7. Explain, with equations, how the nitro group could be introduced into the ring or side chain of toluene.
8. What are drying agents?

## CHAPTER TWENTY

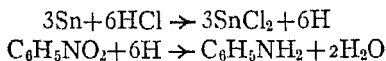
### AMINO COMPOUNDS

THE aromatic amino compounds are those which contain the amino ( $\text{NH}_2$ ) group. The amino group may be introduced into the ring, forming the aryl amines, which are compounds such as **aniline**,  $\text{C}_6\text{H}_5\text{NH}_2$ , or it may enter the side chain, giving compounds such as **benzyl amine**,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ . Compounds containing the amino group in the ring (aryl amines) are prepared by the reduction of nitro compounds. This is the general method which is used to prepare these substances. The reducing agent which is usually used is tin, or iron, and hydrogen chloride, though other reducing agents such as an alcoholic solution of ammonium sulfide are sometimes employed. The simplest of the aromatic amino compounds containing an amino group in the ring is aniline. Aniline was first prepared by Unverdorben, who obtained it by distilling indigo. It is manufactured commercially by reducing nitro benzene with iron and hydrogen chloride. The most convenient laboratory method for the preparation of aniline consists in reducing nitro benzene with tin and hydrogen chloride.

#### EXPERIMENT 68

##### Preparation of aniline, $\text{C}_6\text{H}_5\text{NH}_2$

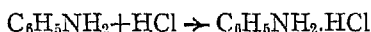
(Amino benzene or phenylamine)



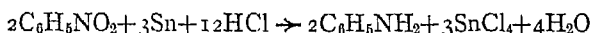
*Materials*  $\left\{ \begin{array}{l} 45 \text{ grams granulated tin} \\ 21 \text{ cc. nitro benzene} \\ 83 \text{ cc. concentrated hydrogen chloride} \\ 75 \text{ grams sodium hydroxide in } 100 \text{ cc. of water} \end{array} \right.$

*Procedure.* Place 45 grams of granulated tin in a liter round flask. Add to this 21 cc. of nitro benzene. Now add gradually 83 cc. of

concentrated hydrogen chloride in 10 cc. portions, in the following manner: Add 10 cc. of the acid, and shake the flask. If the reaction does not begin, warm the flask gently and continue to shake until there is an active evolution of hydrogen gas. If the action becomes too violent, the flask should be immersed in ice water until the reaction has moderated. Continue to add the acid gradually in 10 cc. portions, and occasionally immerse the flask in ice water when the action becomes too violent. When half of the acid has been added the reaction usually takes place rather moderately, and the remainder of the acid may be added in large portions. When the materials have been mixed, connect the flask to a reflux air condenser and heat on a water bath about 40 minutes to effect the complete reduction of the nitro benzene. This may be determined by occasionally removing the stopper from the flask and ascertaining when the odor of nitro benzene is no longer apparent. As shown by the equation, the tin and hydrochloric acid unite to form hydrogen, which reduces the nitro benzene, forming aniline. The aniline thus obtained unites with the excess of hydrogen chloride, forming aniline hydrochloride,  $C_6H_5NH_2.HCl$ :



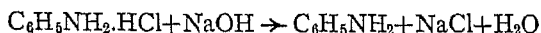
The air condenser is now removed and the flask cooled somewhat. A double salt of stannic chloride and aniline hydrochloride may solidify at this stage of the preparation. This is due to the fact that some stannic chloride is obtained, in accordance with the following equation:



The stannic chloride thus formed unites with the aniline hydrochloride, giving a double salt,



300 cc. of water is now added, after which a solution of 75 grams of sodium hydroxide dissolved in 100 cc. of water is added gradually, until the mixture has an alkaline reaction. The alkali solution decomposes the aniline hydrochloride and any double salts of tin and aniline which may be present, giving free aniline,



The contents of the flask are now steam distilled until the distillate no longer has a milky appearance. Aniline which appears as a color-



less oil passes over with water during the distillation and sinks to the bottom of the receiver under the water. As aniline is somewhat soluble in water, a small amount still remains in the distilling flask. Change the receiver and continue the distillation until about 60 cc. more of the liquid has distilled over. The first and second distillates, consisting of a mixture of aniline and water, are now combined. Add to the combined distillates about 40 grams of sodium chloride. This reduces the solubility of the aniline in water and also the solubility of the ether which is subsequently added. Stir until the salt is dissolved, and pour into a separating funnel. In order to obtain most of the aniline, the mixture should be extracted twice with ether in the following manner: Pour the mixture into a separating funnel, add about 40 cc. of ether, shake, and separate. Pour the top ethereal layer into a dry Erlenmeyer flask. The lower aqueous layer is again poured into a separating funnel, treated with 40 cc. of ether, and separated. The top ethereal layer, which is the second ether extract, is combined with the first ether extract in the Erlenmeyer flask. Add to the combined ether extracts about four sticks (3 cm. in length) of dry, solid potassium hydroxide. The flask is now stoppered firmly and set aside until the next laboratory period, so that the ethereal solution may be completely dehydrated. It frequently happens that the water which is mixed with the ether forms with the potassium hydroxide a small amount of concentrated alkali solution, which sinks to the bottom of the ether solution. The ethereal solution is now filtered into a dry distilling flask, but any heavy layer at the bottom of the ethereal solution should not be allowed to pass through the filter paper. The distilling flask is now connected to a condenser and the excess of ether distilled off over a water bath. The ether thus recovered should be preserved for future use. The water bath is now replaced by a wire gauze and the aniline distilled over a free flame. Collect the fraction boiling between  $180^{\circ}$  and  $185^{\circ}$ . The boiling point of pure aniline is  $183^{\circ}$ . Preserve a specimen and calculate the yield.

Pure aniline is a colorless oil which soon becomes dark in color when exposed to the air. It is very soluble in alcohol, ether, and benzene, but only slightly soluble in water. It has a peculiar odor, is poisonous, and distils easily with steam. The specific gravity of aniline is 1.025 at  $16^{\circ}$ . Aniline is prepared com-

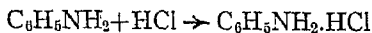
mercially in large quantities and used in the manufacture of dyes, medicinal preparations, and certain aromatic compounds.

The formula of aniline shows that it consists of the phenyl group united to the amino group, and consequently aniline is the amino derivative of benzene (amino benzene) or the phenyl derivative of ammonia (phenyl amine). Aniline is therefore an aromatic primary amine or substituted ammonia. The aromatic amines resemble the aliphatic amines such as methyl amine,  $\text{CH}_3\text{NH}_2$ , in their general chemical behavior, though in certain respects they differ from them.

Aniline unites by addition with acids, forming crystalline salts. Thus the interaction of aniline and hydrogen chloride yields aniline hydrochloride,  $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$ . This is a substituted ammonium salt and is therefore also called *phenyl ammonium chloride*,  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ .

#### EXPERIMENT 69

##### Preparation of aniline hydrochloride, $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$ (Phenyl ammonium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ )



*Materials* { 14 cc. freshly distilled aniline  
14 cc. concentrated hydrogen chloride

*Procedure.* Pour 14 cc. of freshly distilled aniline into a mortar. Add 14 cc. of concentrated hydrogen chloride. The substances are thoroughly mixed by rubbing them together with a pestle. The reaction product is allowed to cool. Treat the salt with a sufficient amount of water (heated to about  $80^\circ$ ) to dissolve it. Add about 2 grams of animal charcoal, stir, and filter. The filtrate is evaporated on a water bath and allowed to crystallize. Aniline hydrochloride is a crystalline substance which melts at  $192^\circ$ . It is known commercially as *aniline salt*. Preserve a specimen.

Aniline hydrochloride, like other salts of aniline, is hydrolyzed by boiling water or decomposed by alkali solutions :

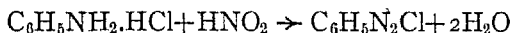


It unites with salts of platinum, tin, and other metals, forming complex double salts, such as  $(\text{C}_6\text{H}_5\text{NH}_2.\text{HCl})_2\text{PtCl}_4$  or  $(\text{C}_6\text{H}_5\text{NH}_2.\text{HCl})_2.\text{SnCl}_4$ .

The aryl amines may be distinguished from the aliphatic amines by their behavior with nitrous acid. In the discussion of the aliphatic amines it was pointed out that when salts of these substances are treated with nitrous acid, alcohols are obtained. Thus methyl amine hydrochloride interacts with nitrous acid, yielding methyl alcohol,

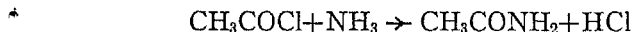


When salts of the aryl amines are treated with nitrous acid at room temperature, alcohols are not obtained, but salts known as *diazo*, or *diazonium*, *compounds* are formed. Thus aniline hydrochloride interacts with nitrous acid, yielding phenyl diazonium chloride,  $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ :



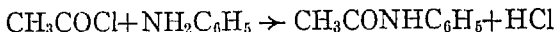
These diazonium compounds will be considered later. They are very active substances and may be converted into various kinds of compounds.

**Derivatives of aniline.** When the hydrogen atoms in the amino group of aniline are substituted by certain groups, various important derivatives of aniline are obtained. In the discussion of the preparation of amides it was stated that they may be prepared by the interaction of acid chlorides and ammonia. Thus acetamide may be obtained by treating acetyl chloride with ammonia :

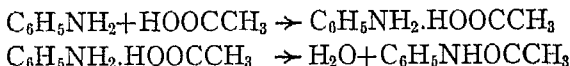


Aniline, being a substituted ammonia, reacts with acid chlorides in a similar manner, yielding substituted amides. Thus aniline

interacts with acetyl chloride, giving acetanilide, (phenyl acetamide)  $\text{CH}_3\text{CONHC}_6\text{H}_5$ :



Acetanilide may be prepared also by boiling aniline with glacial acetic acid for several hours. The aniline acetate which is first formed is decomposed with the elimination of water, yielding acetanilide:

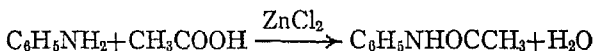


This method of preparing acetanilide may be accelerated by treating the aniline with glacial acetic acid in the presence of anhydrous zinc chloride, which absorbs the water formed in the reaction.

#### EXPERIMENT 70

##### Preparation of acetanilide, $\text{C}_6\text{H}_5\text{NHOCCH}_3$

(Antifebrin or phenyl acetamide)



*Materials*  $\left\{ \begin{array}{l} 10 \text{ cc. aniline (recently distilled)} \\ 14 \text{ cc. glacial acetic acid} \\ 4 \text{ grams anhydrous zinc chloride} \end{array} \right.$

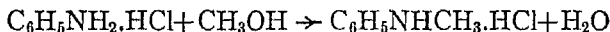
*Procedure.* Pour about 20 cc. of aniline into a 100 cc. distilling flask. Connect the flask to a condenser and distil over about 10 cc. The freshly distilled aniline is now placed in a flask and carefully stoppered. Place 2 grams of anhydrous zinc chloride in a 100 cc. Florence flask, and to this add 10 cc. of the aniline which has just been distilled and 14 cc. of glacial acetic acid. The flask containing the materials is connected to a reflux condenser and boiled gently over a wire gauze about two hours. The apparatus is now disconnected and the reaction product poured slowly, while hot, into a beaker containing about 400 cc. of cold water. Stir the mixture. The acetanilide separates as a solid. Filter, and wash with a small amount of cold water. The product is now placed in a beaker and boiled with

about 200 cc. of hot water to which about 5 grams of animal charcoal has been added. Filter, and cool the filtrate. Acetanilide separates as rhombic plates which melt at  $116^{\circ}$ . Weigh the product obtained, calculate the yield, and preserve a specimen.

Acetanilide crystallizes in glistening plates. It is very soluble in hot water but only slightly soluble in cold water. It is hydrolyzed by alkalis or acids into aniline and acetic acid. Medicinally it is known as *antifebrin* and is used for reducing the temperature of the body in fever cases and as a constituent of headache powders.

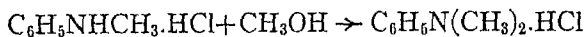
Other anilides may be prepared by methods similar to those used in preparing acetanilide. Thus formanilide,  $C_6H_5NHOCH$ , may be obtained by the interaction of aniline and formic acid. It is a crystalline substance which melts at  $46^{\circ}$ .

When the hydrogen atoms in the amino group of aniline are substituted by alkyl groups, such as methyl or ethyl, secondary and tertiary aromatic amines are obtained. These mixed amines may be prepared by reactions analogous to those used in preparing the aliphatic secondary and tertiary amines. They are manufactured commercially by the interaction of aniline, hydrogen chloride, and the proper alcohol. Thus methyl aniline is obtained in the form of its hydrochloride  $C_6H_5NHCH_3.HCl$  by the interaction of aniline, hydrogen chloride, and methyl alcohol or by simply heating aniline hydrochloride with methyl alcohol,



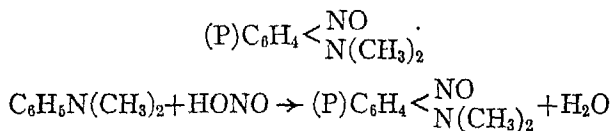
**Methyl aniline**,  $C_6H_5NHCH_3$ , is an oil which boils at  $192^{\circ}$ . It may be obtained from its hydrochloride by treating the latter with an alkali solution, steam distilling, and extracting with ether. It is prepared commercially and used in the manufacture of dyes. Methyl aniline may be regarded as ammonia in which one hydrogen atom has been substituted by the phenyl group and another hydrogen atom substituted by the methyl group. It is therefore an aromatic secondary amine.

**Dimethyl aniline**,  $C_6H_5N(CH_3)_2$ , like methyl aniline is prepared by the interaction of aniline, hydrogen chloride, and methyl alcohol. The hydrochloride of methyl aniline is probably first obtained, and this then reacts with methyl alcohol, yielding the hydrochloride of dimethyl aniline,  $C_6H_5N(CH_3)_2.HCl$ :



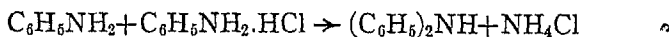
Dimethyl aniline is a colorless oil which boils at  $192^\circ$ . It is manufactured commercially and used extensively in the preparation of dyes. It is an example of an aromatic tertiary mixed amine.

The dialkyl anilines such as dimethyl aniline differ in their chemical behavior from the aliphatic tertiary amines in that they react readily with nitrous acid, yielding *para* compounds containing the nitroso group (NO) and known as *para nitroso compounds*. Thus the interaction of dimethyl aniline and nitrous acid yields *para nitroso dimethyl aniline*,



These *para nitroso* compounds usually have an intensely green color and are important commercially as intermediate products in the manufacture of certain dyes.

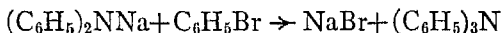
**Diphenyl amine**,  $C_6H_5NHC_6H_5$ , or  $(C_6H_5)_2NH$ , may be regarded as the phenyl derivative of aniline or the diphenyl derivative of ammonia. It is an aromatic secondary amine. It is prepared by heating aniline with aniline hydrochloride at a temperature of about  $200^\circ$ :



It is a crystalline substance which melts at  $54^\circ$  and boils at  $302^\circ$ . It is insoluble in water but dissolves readily in ligroin

and is prepared commercially for use in the manufacture of dyes. When treated with sodium, diphenyl amine yields a sodium derivative known as *sodium diphenyl amine*,  $(\text{C}_6\text{H}_5)_2\text{NNa}$ .

**Triphenyl amine**,  $(\text{C}_6\text{H}_5)_3\text{N}$ , is an aromatic tertiary amine which may be prepared by heating sodium diphenyl amine with phenyl bromide at a temperature of about  $300^\circ$ :



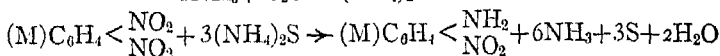
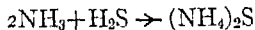
It is a crystalline substance which melts at  $127^\circ$ .

**Nitranilines**,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NH}_2 \\ \text{NO}_2 \end{smallmatrix}$ , are disubstitution products of benzene, or nitro derivatives of aniline. These compounds cannot be prepared by nitrating aniline because it is difficult to control the reaction and obtain only mononitro derivatives of aniline. This difficulty may be overcome if an acetyl radical is introduced into the amino group of aniline. Thus aniline may be converted into acetanilide,  $\text{C}_6\text{H}_5\text{NHOCCH}_3$ , which when nitrated yields ortho and para nitro acetanilides,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NHOCCH}_3 \\ \text{NO}_2 \end{smallmatrix}$ .

These nitro acetanilides may be separated by crystallization. When the ortho and para nitro acetanilides are hydrolyzed, they are converted into the corresponding ortho and para nitranilines,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NH}_2 \\ \text{NO}_2 \end{smallmatrix}$ . Ortho nitraniline crystallizes in yellow needles which melt at  $71^\circ$ . It is very soluble in alcohol but only slightly soluble in cold water. Para nitraniline crystallizes in colorless needles which melt at  $147^\circ$ . Like the ortho compound, it dissolves readily in alcohol but is difficultly soluble in water. When reduced, these substances are converted into the corresponding phenylene diamines,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$ . Meta nitraniline is obtained by the partial reduction of meta dinitro benzene with an alcoholic solution of ammonium sulfide.

## EXPERIMENT 71

Preparation of meta nitraniline,  $(M)C_6H_4<\begin{smallmatrix} NH_2 \\ NO_2 \end{smallmatrix}$



*Materials*  $\left\{ \begin{array}{l} 12 \text{ grams (M) dinitro benzene} \\ 47 \text{ cc. ethyl alcohol (95 per cent)} \\ 7 \text{ cc. concentrated ammonium hydroxide} \\ 200 \text{ cc. hydrogen chloride (1:1)} \end{array} \right.$

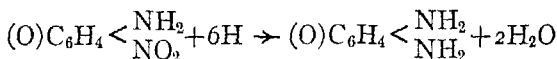
*Procedure.* Place 12 grams of powdered meta dinitro benzene in a 300 cc. flask. To this is added 47 cc. of ethyl alcohol (95 per cent) and 7 cc. of concentrated ammonia water. The mixture is now treated with hydrogen sulfide, which is obtained from the laboratory apparatus or prepared in a separate flask by allowing sulfuric acid (1:3) to drop upon ferrous sulfide.

The hydrogen sulfide gas is washed by passing it through a gas wash bottle containing a small amount of water, after which the washed gas is passed into the dark-red dinitro benzene mixture. Flakes of sulfur gradually separate out, while the dinitro benzene is gradually dissolved. The gas is conducted about 0.5 hour, after which the flask containing the mixture is removed and heated on a water bath a few minutes to a temperature of about 70°. The flask is now cooled and the mixture again saturated with hydrogen sulfide. In order to complete the reaction, warm and saturate with hydrogen sulfide several times. The reaction is probably finished when hydrogen sulfide has been passed into the mixture about 1.5 hours. The reaction product is now treated with water until no further precipitate is obtained, after which it is filtered and the precipitate washed with water. The precipitate is now placed in a flask, treated with about 50 cc. of hot hydrogen chloride (1:1), and the liquid decanted off and filtered. The treatment with hydrogen chloride should be repeated several times in order to dissolve out most of the nitraniline and leave the sulfur and any unchanged dinitro benzene. The filtrate, which is a hydrogen chloride solution of nitraniline, is now treated with ammonia until slightly alkaline. The mixture is cooled and the precipitated nitraniline filtered and purified by crystallization from hot water. It is obtained as yellow needles melting at 114°. Preserve a specimen and calculate the yield.

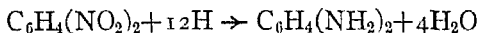


. When meta nitraniline is reduced, it is converted into meta phenylene diamine,  $(M)C_6H_4(NH_2)_2$ .

**Phenylene diamines**, (aromatic diamines)  $C_6H_4<\begin{smallmatrix} NH_2 \\ NH_2 \end{smallmatrix}$ , are diamino derivatives of benzene. The ortho, meta, and para phenylene diamines are obtained by reducing the corresponding ortho, meta, and para nitranilines:



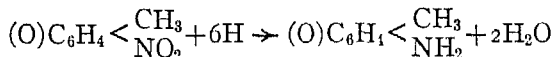
The phenylene diamines may be prepared also by reducing the dinitro benzenes:



These aromatic diamines are colorless solids which are oxidized and become brown when exposed to the air. The ortho compound melts at  $102^\circ$ , the meta at  $63^\circ$ , and the para at  $147^\circ$ . The meta and para compounds are used in the manufacture of dyes.

The table on the following page shows a few of the amino compounds we have studied and also some amino derivatives of toluene.

Amino derivatives of toluene may be obtained by introducing the amino group into the ring, forming the toluidines,  $C_6H_4<\begin{smallmatrix} CH_3 \\ NH_2 \end{smallmatrix}$ , or by allowing the amino group to enter the side chain, giving compounds such as the benzyl amines,  $C_6H_5CH_2NH_2$ . The three toluidines (ortho, meta, and para) are amino derivatives of toluene. They may be obtained by reducing the corresponding ortho, meta, and para nitro toluenes,



The reducing agent which is commonly used is tin and hydrogen chloride. Para toluidine is a crystalline substance which melts at  $45^\circ$  and boils at  $198^\circ$ . The ortho and meta toluidines are oils. The ortho compound boils at  $197^\circ$ , and the meta has a

## COMPOUNDS CONTAINING NITRO AND AMINO GROUPS

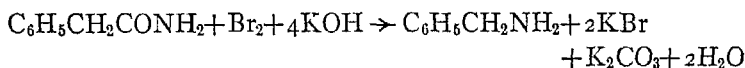
NAME		FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Aniline . . . . .		$C_6H_5NH_2$	-8	183
Aniline hydrochloride . .		$C_6H_5NH_2 \cdot HCl$	192	
Acetanilide . . . . .		$C_6H_5NHOCCH_3$	116	304
Methyl aniline . . . . .		$C_6H_5NHCH_3$		192
Dimethyl aniline . . . . .		$C_6H_5N(CH_3)_2$		192
Diphenyl amine . . . . .		$(C_6H_5)_2NH$	54	302
Triphenyl amine . . . . .		$(C_6H_5)_3N$	127	
Nitrilanines	Ortho	$C_6H_4 \begin{cases} NH_2 & (1) \\ NO_2 & (2) \end{cases}$	71	
	Meta	$C_6H_4 \begin{cases} NH_2 & (1) \\ NO_2 & (3) \end{cases}$	114	
	Para	$C_6H_4 \begin{cases} NH_2 & (1) \\ NO_2 & (4) \end{cases}$	147	
Phenylene diamines	Ortho	$C_6H_4(NH_2)_2$ (1 : 2)	102	
	Meta	$C_6H_4(NH_2)_2$ (1 : 3)	63	
	Para	$C_6H_4(NH_2)_2$ (1 : 4)	147	
Toluidines	Ortho	$C_6H_4 \begin{cases} CH_3 & (1) \\ NH_2 & (2) \end{cases}$		197
	Meta	$C_6H_4 \begin{cases} CH_3 & (1) \\ NH_2 & (3) \end{cases}$		199
	Para	$C_6H_4 \begin{cases} CH_3 & (1) \\ NH_2 & (4) \end{cases}$	45	198
Benzyl amine . . . . .		$C_6H_5CH_2NH_2$		185

boiling point of  $199^{\circ}$ . The ortho and para toluidines are used in preparing dyes. The toluidines resemble aniline in their general chemical behavior. When treated with acids they form salts such as ortho toluidine hydrochloride,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix} \cdot \text{HCl}$ . They react with nitrous acid, yielding diazo compounds, such as para diazo toluene sulfate,  $(\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{N}_2 \end{smallmatrix})_2 \text{SO}_4$ .

**Benzyl amines** are aromatic amines which contain the amino group in the side chain. The simplest of these compounds is benzyl amine,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ . These substances may be prepared by the general methods which are used to prepare the aliphatic amines. Thus benzyl amine may be obtained in the form of its hydrochloride,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \text{HCl}$ , by the interaction of benzyl chloride and alcoholic ammonia,



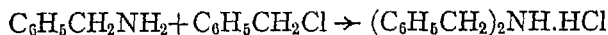
It may be prepared also by treating the amide of phenyl acetic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{CONH}_2$ , with bromine and a solution of potassium hydroxide,



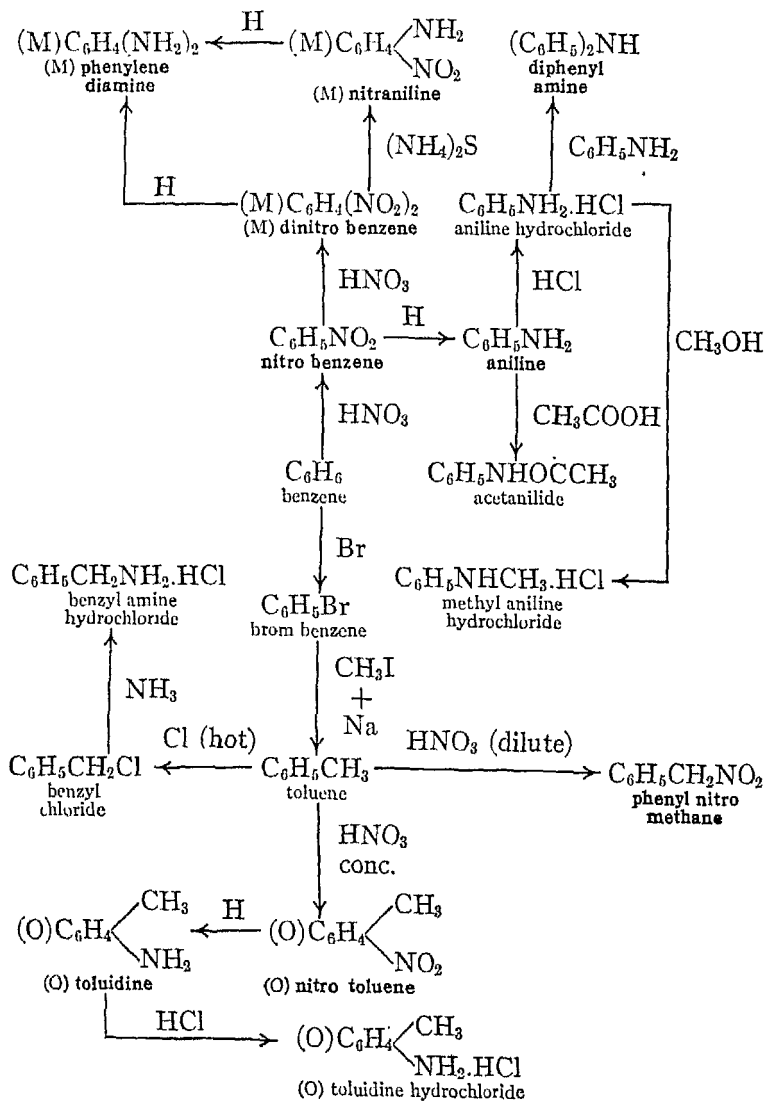
This method of preparation is similar to that used in preparing methyl amine from acetamide (see Experiment 33, page 152).

Benzyl amine is a colorless liquid which has an odor resembling ammonia. It boils at  $185^{\circ}$  and is very soluble in water. When treated with nitrous acid, it does not yield a diazo compound but is converted into benzyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ . In this respect it differs from the aryl amines, which give diazo compounds when treated with nitrous acid.

• Dibenzyl amine,  $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NH}$ , and tribenzyl amine,  $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{N}$ , may be obtained in the form of their salts by heating benzyl amine and benzyl chloride in the proper proportions:



## NITRO AND AMINO COMPOUNDS



Dibenzyl amine is a liquid which boils at  $300^{\circ}$ , and tribenzyl amine is a crystalline substance which melts at  $91^{\circ}$ .

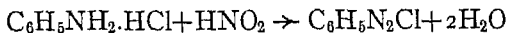
## QUESTIONS

1. Explain, with equations, the preparation of aniline. Having prepared aniline, why is the mixture made alkaline before steam distillation?
2. Give two other names for aniline.
3. Explain, with equations, the preparation of aniline hydrochloride and acetanilide.
4. Write the structural formulas of methyl aniline, dimethyl aniline, diphenyl amine, and triphenyl amine.
5. Explain, with equations, the preparation of meta nitraniline.
6. What compounds are obtained by reducing the nitranilines? Give equations.
7. What compounds are obtained by reducing the nitro toluenes? Give equations.
8. Write the formula of benzyl amine and dibenzyl amine.
9. Outline the following reactions:
  - a. benzene  $\rightarrow$  aniline  $\rightarrow$  acetanilide.
  - b. benzene  $\rightarrow$  toluene  $\rightarrow$  (O) toluidine.
  - c. benzene  $\rightarrow$  (M) phenylene diamine.
10. For what purpose is aniline used?
11. Write the formula of a compound containing the amino group in the ring. Write the formula of another compound which has the amino group in the side chain.
12. A hydrocarbon has the empirical formula  $C_3H_4$ . When nitrated it yields a nitro compound which has the molecular formula  $C_9H_{11}NO_2$ . This nitro compound gives on reduction the amine  $C_9H_{13}N$ . Write the outline equations indicated above. Each of the three compounds above has an isomer. Write the formulas of these isomers.
13. A certain hydrocarbon has the empirical formula  $C_4H_6$ . When it was nitrated and the resulting nitro compound reduced, an amine having the molecular formula  $C_8H_{12}N_2$  was obtained. Write the outline equations indicated above.
14. Two compounds have the same molecular formula. One of them is obtained by treating the acid amide of phenyl acetic acid with a potassium hydroxide solution of bromine. Write an equation showing the preparation of the other compound.

## CHAPTER TWENTY-ONE

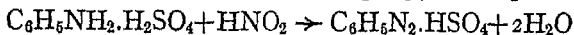
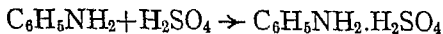
### DIAZONIUM COMPOUNDS

THE diazonium, or diazo, compounds are prepared by treating salts of the aromatic primary amines with nitrous acid. Thus, when a cool aqueous solution of aniline hydrochloride is treated with nitrous acid, phenyl diazonium chloride,  $C_6H_5N_2Cl$ , is obtained. This substance is also known as diazo benzene chloride,



These diazo, or diazonium, compounds are readily soluble in water, but since they are difficultly soluble in alcohol and ether they may be precipitated by these solvents and separated from their aqueous solutions. They are crystalline substances, and when obtained in a thoroughly dry condition are very explosive, though usually they may be handled with comparative safety when moist. The diazo compounds are very active and give characteristic reactions by which they may be converted into various kinds of compounds. They are therefore very important substances in synthetic and technical chemistry. On account of the highly explosive character of these compounds they are not separated from solution but are used in the form of their aqueous solutions to prepare other compounds.

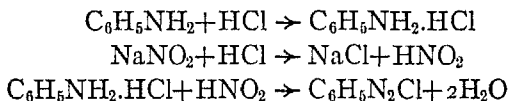
The method of preparing an aqueous solution of a diazonium compound (diazotizing solution) is illustrated by the following procedure, showing the preparation of a solution of phenyl diazonium sulfate,  $C_6H_5N_2.HSO_4$ . A definite quantity of aniline is treated with an aqueous solution of sulfuric acid containing an excess of the calculated quantity of acid. This mixture is cooled by ice water, and to it is added slowly an aqueous solution of sodium nitrite containing the calculated quantity of nitrite:



As shown by the equations above, when aniline is treated with sulfuric acid in excess, the acid aniline sulfate,  $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_2\text{SO}_4$ , is obtained. The excess of sulfuric acid reacts with sodium nitrite, giving nitrous acid. The interaction of nitrous acid and the acid aniline sulfate yields the acid phenyl diazonium sulfate,  $\text{C}_6\text{H}_5\text{N}-\text{OSO}_2\text{OH}$ , or  $\text{C}_6\text{H}_5\text{N}_2 \cdot \text{HSO}_4$ . The neutral phenyl

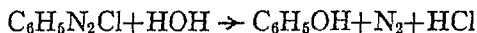


diazonium sulfate would be  $(\text{C}_6\text{H}_5\text{N}_2)_2\text{SO}_4$ . This diazotizing solution is now ready to be used for preparing other substances which are obtained from aniline through the diazo reactions. A diazo solution containing phenyl diazonium chloride,  $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ , may be obtained in a similar manner by diazotizing aniline with hydrogen chloride and sodium nitrite:

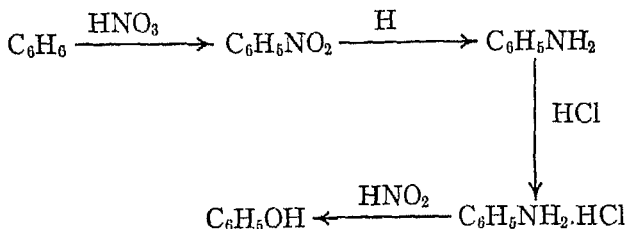


When solutions of diazo salts are treated with certain substances, the diazo group is replaced by other groups. The diazo compounds therefore serve as useful intermediate products in converting aromatic amines into other classes of compounds. The general chemical behavior of diazonium salts is illustrated by the following reactions showing the preparation of various classes of compounds:

1. **Preparation of hydroxyl compounds.** When an aqueous solution of a diazonium salt is boiled with water, the diazo group is replaced by hydroxyl:



Thus phenyl diazonium chloride when hydrolyzed yields phenol,  $\text{C}_6\text{H}_5\text{OH}$ . Since phenyl diazonium chloride is obtained by diazotizing aniline, and aniline may be obtained from benzene, it is evident that reactions of diazonium compounds enable us to introduce the hydroxyl group into aromatic hydrocarbons:



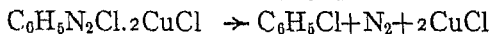
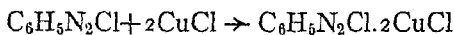
2. **Replacement of the diazo group by hydrogen.** When a diazonium salt (not an aqueous solution of it) is heated with absolute alcohol under certain conditions, the diazo group is replaced by hydrogen:



3. **Preparation of halogen compounds.** Several methods are employed to replace the diazo group by halogens. When a diazonium sulfate solution is warmed with concentrated hydrogen iodide, the diazo group is replaced by iodine:



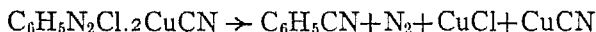
Chlorine or bromine is introduced into a diazo compound in place of the diazo group most conveniently by the Sandmeyer reaction. This consists in treating the diazo salt with a cuprous salt solution. Thus, when a solution of phenyl diazonium chloride is warmed with a cuprous chloride solution which contains hydrogen chloride, the addition product of the diazo salt which is probably first obtained is decomposed, yielding chlor benzene:



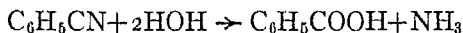
Brom benzene may be obtained in a similar manner by the interaction of a solution of phenyl diazonium chloride and a cuprous bromidesolution:  $\text{C}_6\text{H}_5\text{N}_2\text{Cl}\cdot 2\text{CuBr} \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{N}_2 + \text{CuCl} + \text{CuBr}$ .

4. **Preparation of cyanogen compounds.** When the solution of a diazo salt is warmed with a solution containing cuprous cyanide and potassium cyanide, the diazo group is replaced by the cyanogen group:



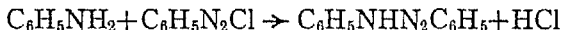


Phenyl cyanide,  $\text{C}_6\text{H}_5\text{CN}$ , behaves like methyl cyanide when hydrolyzed; that is, the cyanogen group is converted into carboxyl:



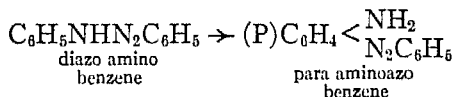
Aromatic carboxyl acids such as benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , may therefore be prepared from diazo compounds.

**Diazo amino compounds.** The diazonium compounds give other characteristic reactions, some of which are of considerable technical importance, as they are used in the manufacture of dyes. Diazo amino benzene,  $\text{C}_6\text{H}_5\text{NHN}_2\text{C}_6\text{H}_5$ , is prepared by treating aniline with phenyl diazonium chloride:



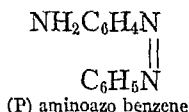
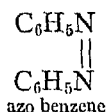
Diazo amino benzene is a yellow crystalline substance which is soluble in ether, alcohol, and benzene. It melts at  $96^\circ$ . A number of other diazo amino compounds may be prepared in accordance with the reaction above by using in place of aniline some other aromatic amine and instead of phenyl diazonium chloride another diazonium salt.

**Aminoazo compounds.** There are several methods which are used for the preparation of aminoazo compounds such as para aminoazo benzene,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NH}_2 \\ \text{N}_2\text{C}_6\text{H}_5 \end{smallmatrix}$ . One of the most interesting of these is the molecular rearrangement of diazo amino compounds. When diazo amino benzene is treated with a small quantity of aniline hydrochloride and warmed to a temperature of about  $40^\circ$ , the diazo amino benzene undergoes an intramolecular change and is converted into para aminoazo benzene:



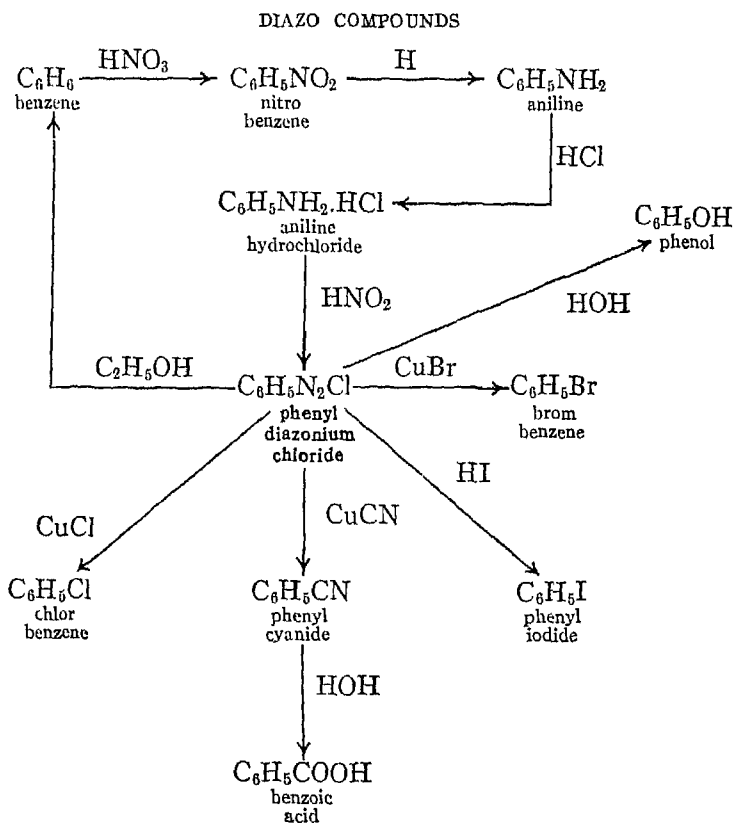
Para aminoazo benzene is obtained from its alcoholic solution as orange-colored crystals which melt at  $126^\circ$ . The relation between azo benzene and aminoazo benzene, which is the amino

derivative of azo benzene, is shown by the following formulas :

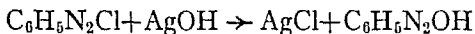


Aminoazo benzene forms brilliantly colored salts which are used as dyes. The yellow dye, "aniline yellow," is the hydrochloride of aminoazo benzene,  $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$ .

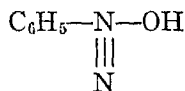
Some of the important diazo reactions are again illustrated by the following outline equations :



. *Structure.* The general behavior of diazonium salts indicates that they resemble the ammonium salts in structure. When a solution of phenyl diazonium chloride is treated with silver hydroxide, a precipitate of silver chloride and an alkaline solution containing phenyl diazonium hydroxide,  $C_6H_5N_2OH$ , is obtained :



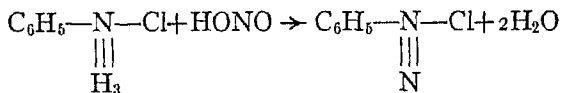
On account of the explosive character of phenyl diazonium hydroxide, it cannot be isolated and is obtained only in aqueous solution. It is believed that in phenyl diazonium hydroxide, which is a strong base, one nitrogen atom has a valence of five and the other a valence of three. The structural formula of this substance would therefore be :



A salt such as phenyl diazonium chloride is regarded as a derivative of phenyl diazonium hydroxide and accordingly has the formula  $C_6H_5-N-Cl$ . This idea of the structure of diazonium

$$\begin{array}{c} ||| \\ N \end{array}$$

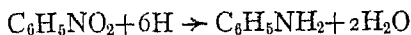
salts agrees in a satisfactory manner with their method of preparation. This is illustrated in the following equation showing the preparation of phenyl diazonium chloride from phenyl ammonium chloride (aniline hydrochloride) :



There are other lines of evidence which suggest that diazonium salts have a structure similar to ammonium salts and contain one atom of nitrogen which has a valence of five.

**Compounds related to the diazonium salts.** As previously stated, nitro compounds are converted into amino compounds by

reduction. Thus aniline is obtained by the reduction of nitrobenzene:

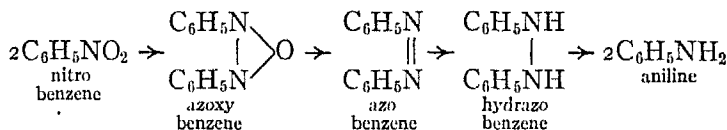


In preparing aniline from nitro benzene, if the experimental conditions are regulated properly and mild reducing agents are

#### DIAZONIUM COMPOUNDS AND RELATED SUBSTANCES

NAME	FORMULA	MELTING POINT, °C.
Phenyl diazonium chloride	$\text{C}_6\text{H}_5\text{N}.\text{Cl}$     N	
Diazo amino benzene	$\text{C}_6\text{H}_5\text{NHN}$    $\text{C}_6\text{H}_5\text{N}$	96
Aminoazo benzene	$\text{N}(\text{H})_2\text{C}_6\text{H}_4\text{N}$ (P)    $\text{C}_6\text{H}_5\text{N}$	126
Azoxy benzene	$\text{C}_6\text{H}_5\text{N}$   $\text{C}_6\text{H}_5\text{N}$ \text{O}	36
Azo benzene	$\text{C}_6\text{H}_5\text{N}$    $\text{C}_6\text{H}_5\text{N}$	68
Hydrazo benzene	$\text{C}_6\text{H}_5\text{NH}$   $\text{C}_6\text{H}_5\text{NH}$	126
Benzidine	$\text{C}_6\text{H}_4\text{NH}_2$   $\text{C}_6\text{H}_4\text{NH}_2$	122
Hydrazine	$\text{NH}_2$   $\text{NH}_2$	1.4
Phenyl hydrazine	$\text{NHC}_6\text{H}_5$   $\text{NH}_2$	23

employed, it is possible to separate out a number of intermediate products, as shown by the following outline:

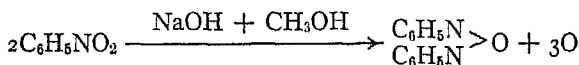


These intermediate products are representative members of classes of compounds known as the *azoxy*, *azo*, and *hydrazo compounds*. These substances and a few other compounds which are related somewhat closely to them are given in the table on the opposite page.

**Azoxy benzene**;  $\text{C}_6\text{H}_5\text{N}(\text{O})\text{NC}_6\text{H}_5$ , is obtained by heating nitro benzene with an alcoholic solution of sodium hydroxide, which is frequently used as a mild reducing agent. The reducing action of the alcoholic solution depends upon the fact that it is oxidized by the oxygen of nitro benzene.

#### EXPERIMENT 72

Preparation of azoxy benzene,  $\begin{array}{c} \text{C}_6\text{H}_5\text{N} \\ | \\ \text{C}_6\text{H}_5\text{N} \end{array} \text{O}$



Materials  $\left\{ \begin{array}{l} 13 \text{ cc. nitro benzene} \\ 120 \text{ cc. methyl alcohol} \\ 19 \text{ grams sodium hydroxide} \end{array} \right.$

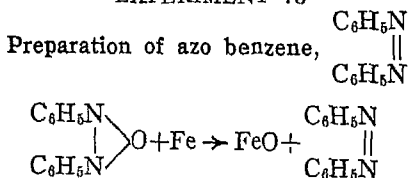
**Procedure.** Place 120 cc. of methyl alcohol in a 250 cc. flask. Add 13 cc. of nitro benzene and 19 grams of sodium hydroxide. The flask containing the mixture is connected to a reflux condenser and heated upon a boiling water bath about 2 hours. Disconnect the flask and pour the reaction product into a 250 cc. distilling flask. The distilling flask is now connected to a condenser and the excess of methyl alcohol distilled off over a water bath. The residue remaining in the flask is now poured into about 300 cc. of ice water. The azoxy benzene separates as a solid or as an oil which solidifies

when the mixture is stirred. Filter, and wash with water. The azoxy benzene is dried on pieces of filter paper, placed in a dry beaker, and treated with a sufficient amount of hot ethyl alcohol to dissolve it. The solution is evaporated somewhat on a water bath and allowed to crystallize. Azoxy benzene crystallizes in yellow needles which melt at  $36^{\circ}$ . Calculate the yield and preserve a small specimen. The remainder of the yield should be used for Experiment 73.

Azoxy benzene is a yellow crystalline compound and is soluble in alcohol and other organic solvents. Energetic reducing agents convert it into aniline.

**Azo benzene**,  $C_6H_5N=NC_6H_5$ , may be obtained by treating nitro benzene with mild reducing agents. It may be prepared also by distilling a mixture of azoxy benzene and iron filings.

#### EXPERIMENT 73



*Materials*  $\left\{ \begin{array}{l} 5 \text{ grams anhydrous azoxy benzene} \\ 15 \text{ grams dry iron filings} \end{array} \right.$

*Procedure.* The azoxy benzene and iron filings used in this experiment should be obtained from the stock room. 5 grams of anhydrous azoxy benzene are placed in a mortar. Add 15 grams of dry iron filings which contain no oil. These materials are mixed intimately by grinding them together in the mortar. The mixture is placed in a 100 cc. distilling flask, and this is connected to an air condenser which is about 30 cm. in length. The reaction product should be distilled over quickly by heating the mixture with a large flame which is rotated constantly. The heating should be continued until the red-colored oil which is obtained no longer distills over. The distillate is collected in a small beaker. If the distillate does not solidify when allowed to cool, the beaker containing it should be immersed in ice water. The solid reddish-brown distillate is washed with a

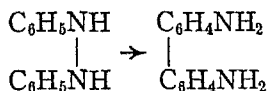
solution of hydrogen chloride (1 : 1) which has been previously cooled by ice water. This removes any aniline which may be present. This mixture is then filtered and the solid distillate washed with ice water, and dried by pressing out on a porous plate or on layers of filter paper. Azo benzene is obtained from the crude distillate by crystallizing from petroleum ether. Azo benzene crystallizes in bright-red crystals which melt at 68°. Calculate the yield and preserve a specimen.

**NOTE.** The anhydrous azoxy benzene which is used in this experiment is prepared by placing azoxy benzene in an evaporating dish and heating on a water bath about 1 hour. As the azoxy benzene has a low melting point, it melts, forming a yellow liquid. The liquid azoxy benzene is converted into solid form by immersing the dish containing it in a vessel of ice water.

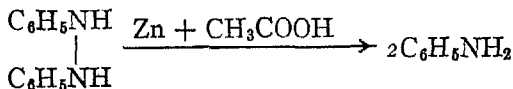
The iron filings should be dry and should contain no grease or oil. They are prepared for use in this experiment by washing with alcohol and ether, and drying in an air bath heated to about 80°, after which they are placed in a dry bottle which is tightly stoppered and set aside until ready for use.

Azo benzene is converted into aniline by active reducing agents. There is a large number of azo compounds, many of which have brilliant colors and are used in the technical manufacture of dyes.

**Hydrazo benzene**,  $C_6H_5NHNHC_6H_5$ , is prepared by reducing nitro benzene, or azo benzene, with mild reducing agents such as an alkaline solution of ammonium sulfide. Hydrazo benzene is a colorless crystalline substance which melts at 126°. When exposed to the air it is slowly oxidized to azo benzene. When treated with strong acids, such as hydrochloric or sulfuric, hydrazo benzene undergoes a molecular rearrangement and is converted into the isomeric benzidine,  $(P)NH_2C_6H_4C_6H_4NH_2$ :



When treated with zinc dust and acetic acid, hydrazo benzene is reduced to aniline:



**Benzidine**, or para diamino diphenyl,  $\begin{array}{c} \text{C}_6\text{H}_4\text{NH}_2 \\ | \\ \text{C}_6\text{H}_4\text{NH}_2 \end{array}$ , is the diamino derivative of diphenyl,  $\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \end{array}$ , which is a double ring compound. Benzidine is a colorless crystalline compound which melts at  $122^\circ$ . It is prepared commercially for use in the manufacture of azo dyes.

**Hydrazines.** Hydrazo benzene,  $\begin{array}{c} \text{C}_6\text{H}_5\text{NH} \\ | \\ \text{C}_6\text{H}_5\text{NH} \end{array}$ , is the diphenyl derivative of hydrazine,  $\begin{array}{c} \text{NH}_2 \\ | \\ \text{NH}_2 \end{array}$ . The monophenyl derivative of hydrazine is known as *phenyl hydrazine*,  $\text{C}_6\text{H}_5\text{NHNH}_2$ , and is prepared in the form of its hydrochloride by the reduction of phenyl diazonium chloride:



Phenyl hydrazine may be obtained from its hydrochloride by treating the latter with an alkali solution:



Phenyl hydrazine is a crystalline substance which melts at  $23^\circ$  and boils at  $243^\circ$ . It dissolves easily in alcohol and ether but is not readily soluble in water. It is a strong base and forms salts such as phenyl hydrazine hydrochloride,  $\text{C}_6\text{H}_5\text{NHNH}_2 \cdot \text{HCl}$ . It reacts readily with aldehydes and ketones, forming phenyl hydrazones, and is used for the detection and separation of sugars.

The synthetic relations between these various substances which are closely related to the diazonium compounds are given in the following outline equations:



$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{N} \\
 | \\
 \text{C}_6\text{H}_5\text{N} \\
 \text{azoxy benzene}
 \end{array}
 \xrightarrow{\text{Fc}}
 \begin{array}{c}
 \text{C}_6\text{H}_5\text{N} \\
 || \\
 \text{C}_6\text{H}_5\text{N} \\
 \text{azo benzene}
 \end{array}
 \xrightarrow{(\text{NH}_4)_2\text{S}}
 \begin{array}{c}
 \text{C}_6\text{H}_5\text{NH} \\
 | \\
 \text{C}_6\text{H}_5\text{NH} \\
 \text{hydrazo benzene}
 \end{array}
 \xrightarrow{\text{HCl}}
 \begin{array}{c}
 \text{C}_6\text{H}_4\text{NH}_2 \\
 | \\
 \text{C}_6\text{H}_4\text{NH}_2 \\
 \text{benzidine}
 \end{array}$$

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{NH} \\
 | \\
 \text{C}_6\text{H}_5\text{NH} \\
 \text{hydrazo benzene}
 \end{array}
 \xrightarrow{\text{Zn} + \text{CH}_3\text{COOH}}
 \begin{array}{c}
 \text{C}_6\text{H}_5\text{NH}_2 \\
 \text{aniline}
 \end{array}
 \xrightarrow{\text{HCl}}
 \begin{array}{c}
 \text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl} \\
 \text{aniline hydrochloride}
 \end{array}$$

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl} \\
 \text{aniline hydrochloride}
 \end{array}
 \xrightarrow{\text{HNO}_2}
 \begin{array}{c}
 \text{C}_6\text{H}_5\text{N}_2\text{Cl} \\
 \text{phenyl diazonium chloride}
 \end{array}$$

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{N}_2\text{Cl} \\
 \text{phenyl diazonium chloride}
 \end{array}
 \xrightarrow{\text{H}}
 \begin{array}{c}
 \text{NHC}_6\text{H}_5 \\
 | \\
 \text{NH}_2 \cdot \text{HCl} \\
 \text{phenyl hydrazine hydrochloride}
 \end{array}$$

$$\begin{array}{c}
 \text{NHC}_6\text{H}_5 \\
 | \\
 \text{NH}_2 \cdot \text{HCl} \\
 \text{phenyl hydrazine hydrochloride}
 \end{array}
 \xrightarrow{\text{NaOH}}
 \begin{array}{c}
 \text{NHC}_6\text{H}_5 \\
 | \\
 \text{NH}_2 \\
 \text{phenyl hydrazine}
 \end{array}$$

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{N}_2\text{Cl} \\
 \text{phenyl diazonium chloride}
 \end{array}
 \xrightarrow{\text{C}_6\text{H}_5\text{NH}_2}
 \begin{array}{c}
 \text{C}_6\text{H}_5\text{NHN} \\
 || \\
 \text{C}_6\text{H}_5\text{N} \\
 \text{diazo amino benzene}
 \end{array}$$

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{NHN} \\
 || \\
 \text{C}_6\text{H}_5\text{N} \\
 \text{diazo amino benzene}
 \end{array}
 \xrightarrow{\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}}
 \begin{array}{c}
 \text{NH}_2\text{C}_6\text{H}_4\text{N} \\
 || \\
 \text{C}_6\text{H}_5\text{N} \\
 \text{(P) amino azo benzene}
 \end{array}$$

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl} \\
 \text{aniline hydrochloride}
 \end{array}
 \xrightarrow{\text{HNO}_2}
 \begin{array}{c}
 \text{C}_6\text{H}_5\text{N}_2\text{Cl} \\
 \text{phenyl diazonium chloride}
 \end{array}$$

$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{N}_2\text{Cl} \\
 \text{phenyl diazonium chloride}
 \end{array}
 \xrightarrow{\text{H}}
 \begin{array}{c}
 \text{NHC}_6\text{H}_5 \\
 | \\
 \text{NH}_2 \cdot \text{HCl} \\
 \text{phenyl hydrazine hydrochloride}
 \end{array}$$

$$\begin{array}{c}
 \text{NHC}_6\text{H}_5 \\
 | \\
 \text{NH}_2 \cdot \text{HCl} \\
 \text{phenyl hydrazine hydrochloride}
 \end{array}
 \xrightarrow{\text{NaOH}}
 \begin{array}{c}
 \text{NHC}_6\text{H}_5 \\
 | \\
 \text{NH}_2 \\
 \text{phenyl hydrazine}
 \end{array}$$

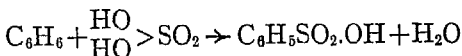
$$\begin{array}{c}
 \text{C}_6\text{H}_5\text{NHN} \\
 || \\
 \text{C}_6\text{H}_5\text{N} \\
 \text{diazo amino benzene}
 \end{array}
 \xrightarrow{\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}}
 \begin{array}{c}
 \text{NH}_2\text{C}_6\text{H}_4\text{N} \\
 || \\
 \text{C}_6\text{H}_5\text{N} \\
 \text{(P) amino azo benzene}
 \end{array}$$

1. How are diazonium compounds prepared?
2. Write equations showing the preparation of phenyl diazonium sulfate and phenyl diazonium chloride.
3. For what purposes are diazonium compounds used?
4. Write balanced equations showing the preparation of phenyl diazonium chloride from benzene.
5. Explain, with outline equations, how phenyl diazonium chloride may be converted into various kinds of compounds.
6. Write the names and formulas of the intermediate products which may be obtained in preparing aniline from nitro benzene.
7. Write the formulas of the following compounds: para aminoazo benzene; benzidine; phenyl hydrazine.
8. Explain how the diazonium salts resemble the ammonium salts in structure.

## CHAPTER TWENTY-TWO

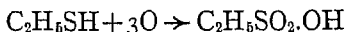
### SULFONIC ACIDS

SULFONIC acids are compounds such as benzene sulfonic acid,  $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$ , which contain the sulfonic acid group ( $\text{SO}_2\text{OH}$ ). The aromatic sulfonic acids are obtained by treating the aromatic hydrocarbons with sulfuric acid. Thus benzene sulfonic acid is obtained by heating benzene with concentrated sulfuric acid :

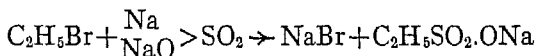


This method of preparing sulfonic acids is known as the *sulfonation process*.

Aliphatic hydrocarbons such as methane and ethane are not acted upon directly by sulfuric acid ; however, aliphatic sulfonic acids may be prepared by oxidizing mercaptans. Thus, when ethyl mercaptan,  $\text{C}_2\text{H}_5\text{SH}$ , is oxidized, ethyl sulfonic acid is obtained :



Ethyl sulfonic acid may be obtained also in the form of its alkali salt by treating an alkyl halogen compound with a sulfite :



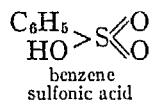
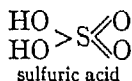
Ethyl sulfonic acid is a thick liquid which crystallizes with difficulty and is soluble in water. A few aliphatic sulfonic acids have been prepared, but, comparatively speaking, they are not compounds of special importance.

As previously stated, one of the principal characteristics of the aromatic hydrocarbons is their reaction with sulfuric acid, yielding sulfonic acids. In this respect the aromatic hydrocarbons behave quite differently from the aliphatic hydrocarbons, which are not acted upon by sulfuric acid. A large number of aromatic sulfonic acids have been prepared, and many of these are compounds of considerable importance, as they are used as

intermediate products for the commercial manufacture of other useful and important compounds.

**Benzene sulfonic acid**,  $C_6H_5SO_2.OH$ , is a crystalline substance which melts at  $50^\circ$  and dissolves readily in water. It is prepared, as stated above, by boiling benzene with concentrated sulfuric acid for several hours until the benzene is dissolved, or it may be obtained by gently heating benzene with fuming sulfuric acid for a shorter period of time.

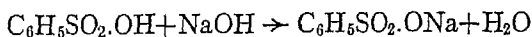
The sulfonation method, which consists in treating an aromatic hydrocarbon with sulfuric acid, is the one which is generally used to prepare the aromatic sulfonic acids. These substances are regarded as derivatives of sulfuric acid obtained by replacing one of the hydroxyl groups of sulfuric acid by an organic radical. The structural formulas of sulfuric acid and benzene sulfonic acid would therefore be as represented below:



The sulfonic acids are usually crystalline compounds which are readily soluble in water. They show the usual properties of strong acids, such as a sour taste and an acid reaction. They decompose carbonates, and when treated with certain metals hydrogen is evolved and the metals are dissolved. In certain respects, however, the sulfonic acids differ from the carboxylic acids in their behavior. The structural formula of benzene sulfonic acid,  $C_6H_5SO_2.OH$ , is written in accordance with its characteristic reactions, which illustrate the general chemical behavior of aromatic sulfonic acids.

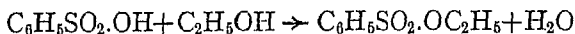
**Derivatives of sulfonic acids.** The sulfonic acids yield derivatives such as salts, esters, and amides similar to those obtained from the carboxylic acids. These sulfonic acid derivatives are obtained by reactions similar to those used in preparing the derivatives of the carboxylic acids.

1. Salts of sulfonic acids are obtained by replacing the hydrogen of the sulfonic acid group by metals. Thus, when an aqueous solution of benzene sulfonic acid is neutralized by a sodium hydroxide solution and the mixture evaporated to dryness, the sodium salt of benzene sulfonic acid, (sodium benzene sulfonate)  $\text{C}_6\text{H}_5\text{SO}_2.\text{ONa}$ , is obtained:



The sodium salt is a crystalline substance.

2. Esters of sulfonic acids are prepared by treating sulfonic acids with alcohols. The interaction of benzene sulfonic acid and ethyl alcohol yields ethyl benzene sulfonate,  $\text{C}_6\text{H}_5\text{SO}_2.\text{OC}_2\text{H}_5$ :

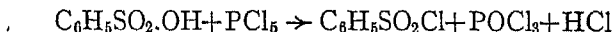


Esters may be obtained also by treating the acid chlorides of sulfonic acids with alcohols:



Ethyl benzene sulfonate is a liquid which boils at  $156^\circ$  (15 mm.).

3. The acid chlorides of sulfonic acids are obtained by treating sulfonic acids or their alkali salts with phosphorus pentachloride. Thus benzene sulfon chloride,  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ , may be prepared by the interaction of benzene sulfonic acid and phosphorus pentachloride:

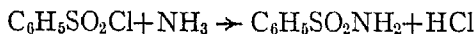


Benzene sulfon chloride is an oil which boils at  $246^\circ$  with decomposition. When immersed in a freezing mixture it solidifies, forming crystals which melt at  $14.5^\circ$ . When boiled with water it is gradually converted into benzene sulfonic acid:



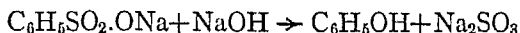
4. Acid amides of sulfonic acids are obtained by the interaction of the acid chlorides of sulfonic acids and concentrated ammonia. Benzene sulfon amide,  $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$ , may be pre-

pared by treating benzene sulfon chloride with concentrated ammonia :



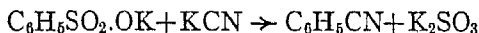
Benzene sulfon amide is a crystalline substance which melts at  $156^\circ$  and is soluble in hot water.

*Reactions.* Under certain conditions the sulfonic acid group may be replaced by other groups. When dry sodium benzene sulfonate is fused with sodium hydroxide, the sulfonic acid group is replaced by hydroxyl, giving phenol,  $\text{C}_6\text{H}_5\text{OH}$  :



Certain phenols are prepared more conveniently by this method than by using the diazo reaction.

Nitriles are obtained by the interaction of a sulfonic acid salt and potassium cyanide. Thus, when dry potassium benzene sulfonate is distilled with potassium cyanide, phenyl cyanide, (benzo nitrile)  $\text{C}_6\text{H}_5\text{CN}$ , is obtained :

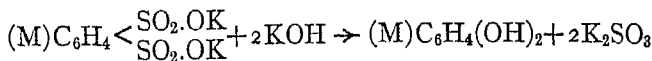


As phenyl cyanide may be hydrolyzed into benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , it is evident that the sulfonic acid reactions may be used to prepare aromatic acids.

As the sulfonic acids may be converted into other kinds of substances, they are used considerably for the preparation of other compounds. The number of sulfonic acid groups which may be introduced into a compound depends upon the kind of substance which is to be sulfonated, on the temperature and concentration of the acid, and on the length of time allowed for sulfonation.

α **Meta benzene disulfonic acid**,  $(\text{M})\text{C}_6\text{H}_4(\text{SO}_2.\text{OH})_2$ , is prepared by treating benzene with a larger quantity of sulfuric acid than is used in making benzene sulfonic acid. It is a crystalline substance. When the neutral potassium salt of this acid is

fused with potassium hydroxide, meta hydroxy benzene, (resorcinol)  $(M)C_6H_4(OH)_2$ , is obtained :

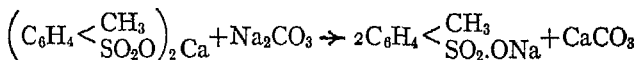
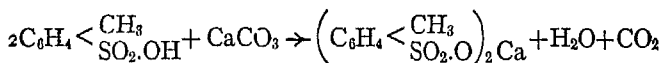
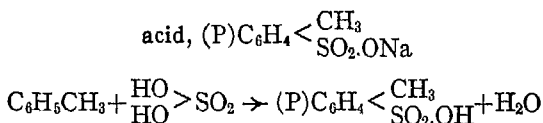


When benzene and sulfuric acid are mixed in the proper proportions and heated under the proper conditions, benzene trisulfonic acid,  $C_6H_3(SO_2.OH)_3$  (1, 3, 5), which is a crystalline substance, is obtained.

When toluene is heated with concentrated sulfuric acid, a mixture of *ortho* and *para* toluene sulfonic acids,  $C_6H_4 < \begin{smallmatrix} CH_3 \\ SO_2.OH \end{smallmatrix}$ , is obtained. By arranging properly the experimental conditions, the reaction product may be made to consist largely of only the *ortho* or *para* compound.

#### EXPERIMENT 74

##### Preparation of the sodium salt of *para* toluene sulfonic acid, $(P)C_6H_4 < \begin{smallmatrix} CH_3 \\ SO_2.ONa \end{smallmatrix}$



*Materials*  $\left\{ \begin{array}{l} 20 \text{ cc. toluene} \\ 40 \text{ cc. concentrated sulfuric acid} \\ \text{Powdered calcium carbonate} \\ \text{Powdered sodium carbonate} \end{array} \right.$

*Procedure.* Pour 20 cc. of toluene in a liter round flask and gradually add 40 cc. of concentrated sulfuric acid. Heat on a water bath about 2 hours, shaking the flask frequently. When all the toluene has dissolved and the solution appears to be homogeneous, pour

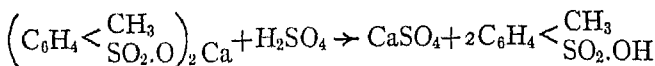
the contents of the flask into a 2-liter evaporating dish containing about 1 liter of water. Powdered calcium carbonate is now added, with constant stirring. This reacts with the toluene sulfonic acid, forming the soluble calcium toluene sulfonate,  $\left(\text{C}_6\text{H}_4\text{SO}_2\text{OCH}_3\right)_2\text{Ca}$ , and also neutralizes the excess of sulfuric acid, precipitating calcium sulfate:



The mixture is now filtered through a muslin filter which is placed over a beaker of 1-liter capacity. The filtrate containing the soluble calcium toluene sulfonate is now evaporated to a volume of about 200 cc. and filtered through filter paper to eliminate the calcium sulfate, which, being somewhat soluble, separates out as a white precipitate on concentrating the solution. A concentrated solution of sodium carbonate is now added in sufficient amount to precipitate exactly the calcium as calcium carbonate and form the sodium salt of para toluene sulfonic acid. The mixture is now filtered through a muslin filter, after which it is again filtered through filter paper and the filtrate evaporated and allowed to crystallize. The crystals are filtered off and treated with a sufficient amount of hot water to dissolve them. Add about 3 grams of animal charcoal, boil, filter, and allow the filtrate to crystallize. The purified crystals of sodium toluene sulfonate are filtered off and dried on pieces of filter paper. Calculate the yield and preserve a specimen.

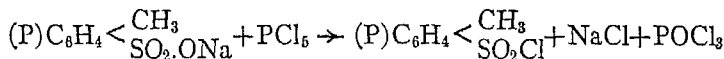
The preparation of the sodium salt of para toluene sulfonic acid illustrates one of the most convenient methods used for the preparation of the aromatic sulfonic acids or their salts. As explained in the preceding experiment, toluene sulfonic acid is obtained by the interaction of toluene and sulfuric acid. The excess of sulfuric acid in the mixture is neutralized by calcium carbonate, forming calcium sulfate. The calcium carbonate also reacts with the sulfonic acid, forming the soluble calcium toluene sulfonate. The mixture is filtered from the insoluble calcium sulfate. The calcium toluene sulfonate which is present in the filtrate may be converted into toluene sulfonic acid by adding an aqueous solution of sulfuric acid containing the cal-

culated amount of sulfuric acid necessary to precipitate exactly the calcium as calcium sulfate :

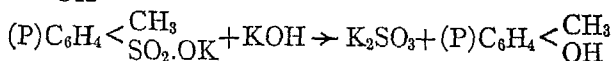


The free para toluene sulfonic acid is obtained by filtering off the insoluble calcium sulfate and evaporating the filtrate. If it is desired to convert the calcium salt into the sodium salt of toluene sulfonic acid, it is treated with sodium carbonate, which precipitates calcium carbonate. This is filtered off, and the sodium toluene sulfonate is obtained by evaporating the filtrate.

Para toluene sulfonic acid is a crystalline substance which melts at  $92^\circ$ . It gives the usual characteristic reactions of sulfonic acids and yields derivatives similar to those obtained from benzene sulfonic acid. Para toluene sulfon chloride,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{SO}_2\text{Cl} \end{smallmatrix}$ , is obtained by the interaction of sodium toluene sulfonate and phosphorus pentachloride :

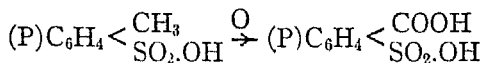


It is a crystalline substance which melts at  $69^\circ$ . Para toluene sulfon amide,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{SO}_2\text{NH}_2 \end{smallmatrix}$ , prepared by treating para toluene sulfon chloride with ammonia, is a crystalline compound melting at  $137^\circ$ . When the potassium salt of para toluene sulfonic acid is fused with potassium hydroxide, para cresol,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{OH} \end{smallmatrix}$ , is obtained :



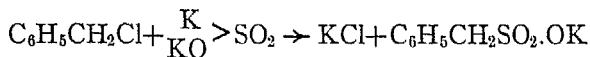
When para toluene sulfonic acid is oxidized with an alkaline solution of potassium permanganate, the methyl group exhibits the usual behavior of an alkyl side chain group and is converted into carboxyl, yielding para sulfo benzoic acid,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{COOH} \\ \text{SO}_2.\text{OH} \end{smallmatrix}$  :





Para sulfo benzoic acid is an example of a compound which contains both the carboxyl and sulfonic acid groups (see Sulfo benzoic acids, page 411).

The sulfonic acid group may be introduced into the side chain of toluene by reactions similar to those employed in preparing alkyl sulfonic acids. Thus benzyl sulfonic acid,  $C_6H_5CH_2SO_2.OH$ , may be obtained in the form of its potassium salt by treating benzyl chloride with potassium sulfite:

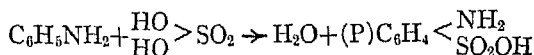


Benzyl sulfonic acid and its potassium salt are crystalline compounds.

**Substituted sulfonic acids.** In the study of the aliphatic carboxyl acids, such as acetic acid,  $CH_3COOH$ , it was pointed out that these compounds consist of an alkyl radical united to the carboxyl group. Acid derivatives such as sodium acetate,  $CH_3COONa$ , are obtained by substituting in the carboxyl group, while substituted acids like monochlor acetic acid,  $CH_2 < \begin{smallmatrix} Cl \\ COOH \end{smallmatrix}$ , are obtained by substitution in the alkyl radical. The aromatic sulfonic acids, like the aliphatic carboxyl acids, yield also substituted acids. **Sulfanilic acid**, (para amino benzene sulfonic acid)  $(P)C_6H_4 < \begin{smallmatrix} NH_2 \\ SO_2.OH \end{smallmatrix}$ , is an example of a substituted sulfonic acid. It is the amino derivative of benzene sulfonic acid, or it may be regarded as the sulfonic acid derivative of aniline. It is prepared by heating aniline with sulfuric acid. When aniline is treated with sulfuric acid in the proper proportions, it forms either the acid aniline sulfate,  $C_6H_5NH_2.H_2SO_4$ , or the neutral aniline sulfate,  $(C_6H_5NH_2)_2H_2SO_4$ . Under certain conditions, however, aniline reacts with sulfuric acid, yielding sulfanilic acid.

## EXPERIMENT 75

Preparation of sulfanilic acid,  $(P)C_6H_4 < \begin{smallmatrix} NH_2 \\ SO_2.OH \end{smallmatrix}$

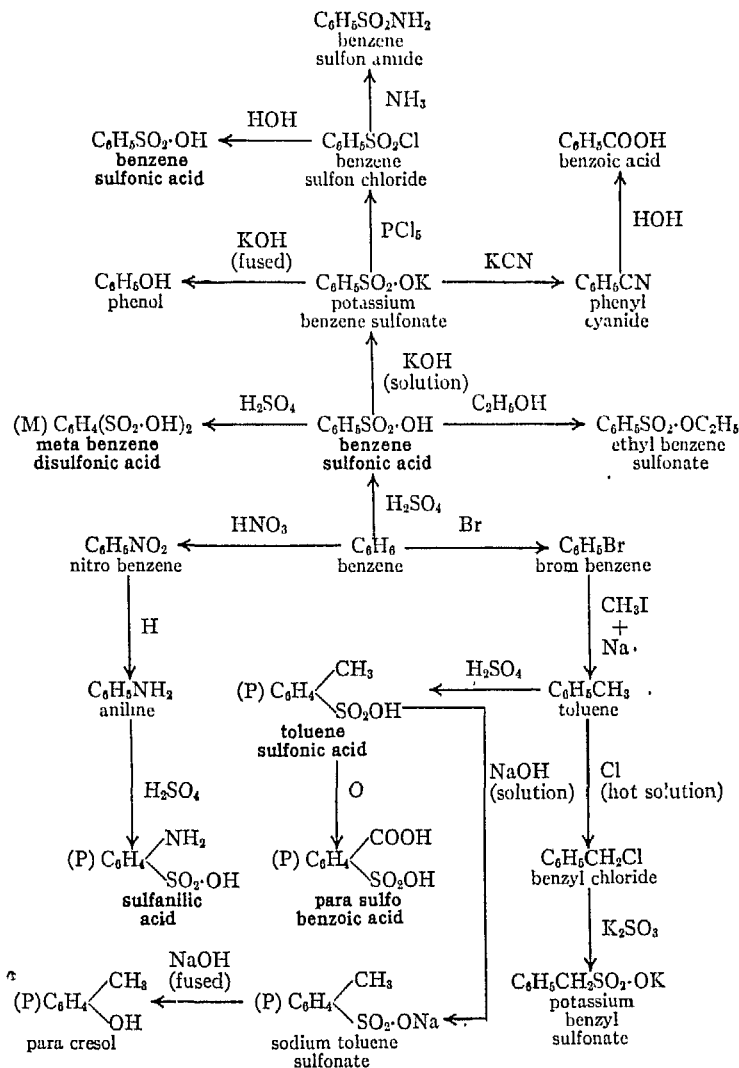


*Materials*  $\left\{ \begin{array}{l} 15 \text{ cc. aniline} \\ 27 \text{ cc. concentrated sulfuric acid} \end{array} \right.$

*Procedure.* Pour 15 cc. of aniline into a 150 cc. round flask. Add gradually 27 cc. of concentrated sulfuric acid. Connect the flask to a reflux air condenser, and immerse it in an oil bath. The oil bath is heated to a temperature of  $180^\circ$  and the heating continued about 4 hours at this temperature, until the reaction is complete. This may be determined by dissolving a small amount of the mixture in water and adding a few cc. of a solution of sodium hydroxide. If the reaction is complete, no aniline separates. The reaction product is poured into about 200 cc. of cold water. The sulfanilic acid is precipitated as a gray crystalline mass. Filter, and wash with a small amount of cold water. The product is now dissolved in hot water; a small amount of animal charcoal (about 3 grams) is added, and the mixture boiled and filtered. The filtrate is crystallized and the crystals filtered and dried on layers of filter paper. Calculate the yield and preserve a specimen.

Sulfanilic acid crystallizes with two molecules of water. It dissolves readily in hot water but is only difficultly soluble in cold water. It is an amino acid containing both a basic ( $NH_2$ ) and an acid ( $SO_2.OH$ ) group. As the acid properties are decidedly more prominent than the basic properties, it forms salts with bases but not with acids. In this respect it differs from amino acetic acid, which forms salts with bases and also with acids. Sulfanilic acid is used in the technical manufacture of certain dyes. The isomeric ortho, and meta, amino benzene sulfonic acids are prepared by reducing the corresponding nitro benzene sulfonic acids,  $C_6H_4 < \begin{smallmatrix} NO_2 \\ SO_2.OH \end{smallmatrix}$ .

## SULFONIC ACIDS



## QUESTIONS

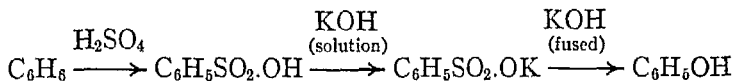
1. What characteristic group do the sulfonic acids contain?
2. Write an equation showing the preparation of ethyl sulfonic acid.
3. What is meant by the "sulfonation process"?
4. From what substance are the sulfonic acids derived?
5. What are the general properties of the sulfonic acids?
6. Write equations showing the preparation of the following compounds: sodium benzene sulfonate; ethyl benzene sulfonate; benzene sulfon chloride; benzene sulfon amide; phenol.
7. Explain, with equations, the preparation of sodium toluene sulfonate; of toluene sulfonic acid.
8. Write formulas of the following compounds: ortho toluene sulfon chloride; para toluene sulfon amide; para sulfo benzoic acid; benzyl sulfonic acid.
9. How is sulfanilic acid prepared?
10. Write equations showing how the sulfonic acid group may be introduced into the ring or into the side chain of toluene.
11. Write the outline equations indicated:
  - a. benzene sulfonic acid  $\rightarrow$  benzoic acid.
  - b. benzene  $\rightarrow$  sulfanilic acid.
  - c. toluene  $\rightarrow$  para sulfo benzoic acid.
  - d. benzene  $\rightarrow$  potassium benzyl sulfonate.
12. Explain, with equations, the laboratory preparation of benzene sulfonic acid.

## CHAPTER TWENTY-THREE

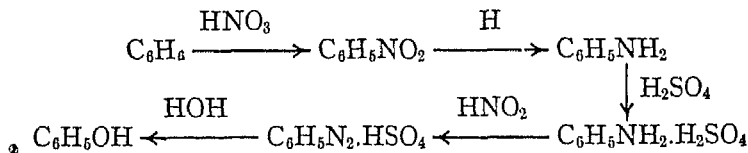
### PHENOLS

THERE are two classes of aromatic hydroxyl compounds. Those such as phenol,  $C_6H_5OH$ , and cresol,  $C_6H_4<\overset{CH}{OH^3}$ , which have the hydroxyl group in the ring, are known as *phenols*. Compounds such as benzyl alcohol,  $C_6H_5CH_2OH$ , which contain the hydroxyl group in the side chain, are called *aromatic alcohols*. These two classes of aromatic hydroxyl compounds behave quite differently in certain respects.

The simplest phenol is the monohydroxy derivative of benzene, which is known as *phenol*, (carbolic acid)  $C_6H_5OH$ . It occurs in coal tar, from which the commercial supply of phenol is obtained. Reactions showing the methods of preparation and general chemical behavior of phenol illustrate in a general manner the chemistry of this class of compounds. Phenol may be prepared in the laboratory from benzene by means of the sulfonic acid reactions:



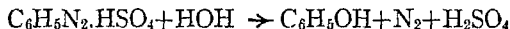
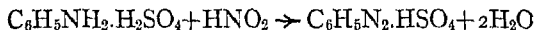
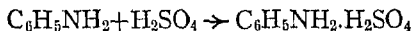
It may be obtained also from benzene by a series of reactions in which nitro benzene, aniline, and phenyl diazonium sulfate are intermediate products:



## EXPERIMENT 76

Preparation of phenol,  $C_6H_5OH$ 

(Carbolic acid)



*Materials* { 22 cc. concentrated sulfuric acid in 100 cc. water  
 19 cc. freshly distilled aniline  
 17.0 grams sodium nitrite in 60 cc. water

*Procedure.* Distil about 30 cc. of aniline. The freshly distilled aniline is poured into a dry Erlenmeyer flask, which is stoppered and kept in a dark place until ready for use. Pour 100 cc. of water into a liter round flask, and add gradually, with constant stirring, 22 cc. of concentrated sulfuric acid. To the hot acid solution add gradually, with constant stirring, 19 cc. of the recently distilled aniline. The aniline reacts with the sulfuric acid, forming acid aniline sulfate,  $C_6H_5NH_2 \cdot H_2SO_4$ . 200 cc. of water is now added and the mixture cooled, after which a solution containing 17 grams of sodium nitrite dissolved in 60 cc. of water is added. The sodium nitrite reacts with the excess of sulfuric acid present, forming nitrous acid. The interaction of nitrous acid and the acid aniline sulfate yields the acid phenyl diazonium sulfate,  $C_6H_5N_2 \cdot HSO_4$ . What is the formula of the neutral phenyl diazonium sulfate? The diazonium sulfate solution thus obtained is warmed for about an hour on a water bath heated to about  $45^\circ$ . The water in the water bath is now heated to the boiling temperature to complete the hydrolysis of the diazonium salt. About 100 cc. of water is now added and the mixture steam distilled. Continue the distillation until about 250 cc. of distillate has been obtained. The distillate is treated with about 40 grams of sodium chloride and poured into a separating funnel. Add about 40 cc. of ether, shake, and separate. The top ethereal layer, containing the phenol, is poured into an Erlenmeyer flask, which is firmly stoppered. The lower aqueous layer is again extracted with about 40 cc. of ether, separated, and the second ether extract poured into the Erlenmeyer flask which contains the first extract. About 5 grams of fused sodium sulfate are now added to dehydrate the ethereal

solution and the mixture allowed to stand several hours. Filter into a 200 cc. distilling flask, attach the flask to a condenser, and distil off the ether on a water bath. The water bath is now removed, a wire gauze placed under the flask, and the phenol distilled over. Collect the fraction boiling between  $176^{\circ}$  and  $185^{\circ}$ . The boiling point of phenol is  $183^{\circ}$ . Preserve a specimen and calculate the yield.

*Caution!* Great care should be taken to prevent the phenol from coming into contact with the hands, as it produces painful burns.

The reactions of phenol with bromine and ferric chloride are used as tests for phenol.

A. Prepare a dilute aqueous solution of phenol by dissolving 0.5 cc. of phenol in about 25 cc. of water. To 2 cc. of this solution add bromine water slowly. A white precipitate is obtained. The further addition of bromine water precipitates tribrom phenol,  $C_6H_2(OH)Br_3$  (2, 4, 6). The precipitate appears to be white, though it is slightly yellow. Tribrom phenol is a crystalline substance which melts at  $92^{\circ}$  and has a characteristic odor.

B. Add a few drops of a ferric chloride solution (1:10) to about 2 cc. of the aqueous solution of phenol prepared in the preceding experiment. A violet color is produced.

Phenol forms colorless crystals which melt at  $42^{\circ}$  and turn pink or red when exposed to air and light. It has a characteristic odor, is very poisonous, and has a corrosive action on the skin, causing painful burns. The painful effects of burns caused by phenol may be relieved considerably by washing immediately with ethyl alcohol and afterwards with water. It dissolves readily in various organic solvents, such as alcohol and ether, but is not very soluble in water (1 part of phenol dissolves in 15 parts of water). It is a strong antiseptic and formerly was used considerably in surgery. At present it is used as a disinfectant, and is employed in the manufacture of picric acid, certain dyes, and medicinal preparations.

**Reactions of phenol.** Like the other members of this class of compounds, phenol gives characteristic reactions when treated with certain substances.

1. Phenol has the properties of an acid, and hence it was called originally *carbolic acid*. Its acid properties, however, are so weak that it does not decompose alkali carbonates, but when treated with an alkali hydroxide solution it is neutralized, forming a salt of phenol. Thus, when phenol is treated with a solution of sodium hydroxide, sodium phenolate,  $\text{C}_6\text{H}_5\text{ONa}$ , is obtained:

$$\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O}$$

Sodium phenolate may be prepared also by treating phenol with sodium. The phenolates are sometimes called *phenates* or *phenoxides*.

2. The chemical behavior of phenol shows that it contains the hydroxyl group and reacts like an alcohol. As shown by the reaction above, phenol yields compounds such as potassium phenolate,  $\text{C}_6\text{H}_5\text{OK}$ , and sodium phenolate,  $\text{C}_6\text{H}_5\text{ONa}$ , in which the hydrogen of the hydroxyl group has been replaced by a metal.

When treated with acid chlorides phenol behaves like ethyl alcohol and forms esters. Thus, when phenol is treated with acetyl chloride, phenyl acetate,  $\text{CH}_3\text{COOC}_6\text{H}_5$ , is obtained:

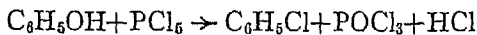


For what purpose is acetyl chloride used?

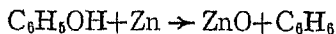
3. Alkali salts of phenol react with alkyl halogen compounds, giving ethers. The interaction of sodium phenolate and methyl iodide yields the mixed ether anisol,  $\text{C}_6\text{H}_5\text{OCH}_3$ , (phenyl methyl ether):



4. When phenol is treated with phosphorus pentachloride, the hydroxyl group is replaced by chlorine, but on account of side reactions the yield of phenyl chloride thus obtained is usually very small:



5. Phenols are reduced to hydrocarbons when distilled over zinc dust:



In this respect they behave quite differently from alcohols.

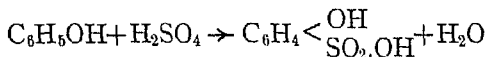


Phenol contains the tertiary alcohol group (COH). When oxidized, phenol yields neither aldehydes nor ketones and in this respect resembles a tertiary alcohol. What is formed by the oxidation of primary alcohols and of secondary alcohols?

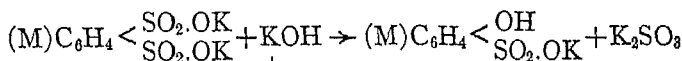
**Substitution products of phenol.** Phenol reacts with various substances, yielding substitution products.

Halogen-substitution products of phenol, such as the chlorine or bromine derivatives, are formed easily by treating phenol with these substances. The interaction of phenol and bromine, for instance, yields the ortho and para brom phenols. The continued addition of bromine to phenol gives dibrom, and finally tribrom, phenol,  $C_6H_2(OH)Br_3$  (Experiment 76, page 362). The monohalogen derivatives of phenol may be prepared also from the corresponding amino phenols,  $C_6H_4<\begin{smallmatrix} NH_2 \\ OH \end{smallmatrix}$ , by means of the diazo reactions.

**Phenol sulfonic acids,**  $C_6H_4<\begin{smallmatrix} SO_2.OH \\ OH \end{smallmatrix}$ . The interaction of phenol and concentrated sulfuric acid yields a mixture of ortho and para phenol sulfonic acids:



At ordinary temperatures the yield consists largely of the ortho compound. At higher temperatures the ortho compound undergoes a molecular rearrangement and is converted into the para compound. Para phenol sulfonic acid may therefore be obtained by heating a mixture of phenol and concentrated sulfuric acid in the proper proportions at a temperature of about  $100^\circ$ . Meta phenol sulfonic acid is prepared in the form of its potassium salt by heating carefully and under the proper conditions a mixture of potassium hydroxide and the potassium salt of meta benzene disulfonic acid:



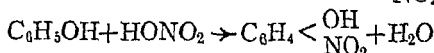
The phenol sulfonic acids show the characteristic behavior of compounds containing the sulfonic acid group and the phenol hydroxyl group. Ortho phenol sulfonic acid has stronger anti-septic and disinfectant properties than phenol. It is manufactured commercially and sold under the name of "aseptol."

**Nitro phenols,**  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{NO}_2 \end{smallmatrix}$ . Phenols are nitrated easily. When phenol is treated with dilute nitric acid, a mixture of ortho and para nitro phenols is obtained. Since only the ortho nitro phenol is volatile with steam, the mixture may be separated by steam distillation.

#### EXPERIMENT 77

Preparation of ortho nitro phenol,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{NO}_2 \end{smallmatrix}$ ,

and para nitro phenol,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{NO}_2 \end{smallmatrix}$



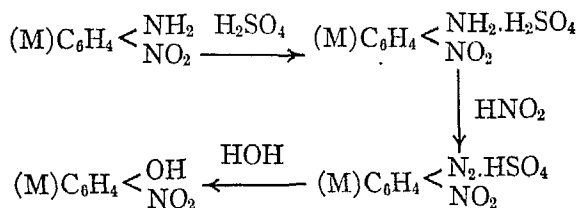
*Materials*  $\left\{ \begin{array}{l} 35 \text{ grams of phenol} \\ 44 \text{ cc. concentrated nitric acid in 150 cc. water} \end{array} \right.$

*Procedure.* Prepare a dilute solution of nitric acid by dissolving 44 cc. of concentrated nitric acid in 150 cc. of water, and pour this solution into a liter round flask. Weigh out 35 grams of phenol in a beaker. (*Caution!* Do not get the phenol on your hands, as it causes painful burns.) The beaker containing the phenol is warmed somewhat, and when the phenol has melted to a liquid it is gradually added to the nitric acid solution, with constant shaking and cooling. During this mixing operation the temperature of the mixture should not rise above  $30^\circ$ . Allow the mixture to stand over night. The product of the reaction settles at the bottom of the flask as a dark oil or solid. The supernatant aqueous solution is poured off, and the reaction product washed several times by pouring water into the flask, shaking somewhat, and carefully pouring off the water. About 500 cc. of water is now added and the mixture steam distilled. The ortho compound is volatile with steam and passes over as a yellow oil of condenses as a yellow solid in the condenser tube. The solid material may be removed from the condenser by turning off the supply of cold water and allowing the water in the condenser to become warm.

When no more of the ortho compound passes over, the distillation is discontinued. The residue remaining in the flask contains the para compound, while the distillate contains the ortho compound. If the distillate consists of a yellow oil, this may be changed to a solid by immersing the beaker which contains it in ice water and stirring the distillate rapidly for a few minutes. The distillate is filtered and the ortho compound dried on filter paper. It may be recrystallized by dissolving in a mixture consisting of 2 parts of ethyl ether and 1 part of petroleum ether, evaporating off a part of the solvent on a water-bath, and allowing to crystallize. Ortho nitro phenol is a yellow crystalline compound which melts at  $45^{\circ}$ .

To obtain the para compound, the product remaining in the distilling flask is heated with about 200 cc. of boiling water and filtered from tarry products. The filtrate is boiled with animal charcoal, which removes part of the coloring matter, and filtered. The colored solution thus obtained is evaporated and allowed to crystallize. The para compound may be recrystallized from hot water. When purified properly, it is obtained as colorless crystals which melt at  $114^{\circ}$ . Preserve specimens of the ortho and para nitro phenols.

Meta nitro phenol is not obtained by the interaction of phenol and nitric acid. It may, however, be prepared from meta nitraniline,  $(M)C_6H_4<\begin{smallmatrix} NH_2 \\ NO_2 \end{smallmatrix}$ , by means of the diazo reaction:

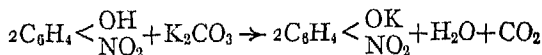


In preparing meta nitro phenol from meta nitraniline, how would you prepare the diazonium solution which is to be hydrolyzed to meta nitro phenol? Meta nitro phenol is a yellow crystalline substance which melts at  $96^{\circ}$ .

The nitro phenols have stronger acid properties than the phenols. This is shown by the fact that they dissolve carbonates, forming salts of the nitro phenols.

## EXPERIMENT 78

Preparation of the potassium salt of ortho nitro phenol  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OK} \\ \text{NO}_2 \end{smallmatrix}$   
 (Ortho potassium nitro phenolate)



*Materials*  $\left\{ \begin{array}{l} 4 \text{ grams ortho nitro phenol} \\ 2 \text{ grams anhydrous potassium carbonate} \end{array} \right.$

*Procedure.* Dissolve 2 grams of powdered anhydrous potassium carbonate in hot water. To this solution add 4 grams of powdered ortho nitro phenol. Evaporate the solution somewhat, and allow it to crystallize. The dark-red crystals of ortho potassium nitro phenolate which are obtained are filtered off and dried on layers of filter paper. Preserve a specimen.

**Picric acid**, (trinitro phenol)  $\text{C}_6\text{H}_2\text{OH}(\text{NO}_2)_3$  (1, 2, 4, 6). When various organic materials such as aniline, silk, wool, or resins are treated with concentrated nitric acid, complex reactions take place and picric acid is one of the products obtained. It may be prepared by heating ortho, or para, nitro phenol with nitric acid, though it is obtained more easily by the interaction of phenol and nitric acid.

Picric acid is a pale-yellow crystalline substance which melts at  $122^\circ$ . It dissolves readily in alcohol and ether. It is difficultly soluble in cold water, though it is fairly soluble in hot water. Aqueous solutions of picric acid have a bitter taste and an acid reaction. They dye silk and wool a yellow color without the aid of a mordant (substantive dye). Picric acid is one of the oldest of synthetic organic dyes.

When treated with certain aromatic hydrocarbons such as benzene or anthracene, picric acid forms crystalline compounds which are decomposed by ammonia. It may therefore be used for the separation and identification of these hydrocarbons.

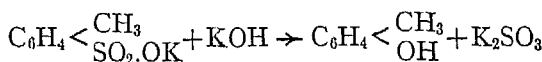
Salts of picric acid such as sodium picrate,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{ONa}$ , explode violently when heated or subjected to percussion. Am-

monium picrate is exceedingly explosive. These salts are used in the manufacture of various explosives such as melinite or lyddite. Picric acid burns quietly when ignited and does not explode when struck. It may, however, be detonated by certain substances.

**Amino phenols**,  $C_6H_4 < \begin{smallmatrix} OH \\ NH_2 \end{smallmatrix}$ . The three amino phenols (ortho, meta, and para) are obtained by reducing the corresponding nitro phenols,  $C_6H_4 < \begin{smallmatrix} OH \\ NO_2 \end{smallmatrix}$ . The amino phenols are usually soluble in water, and when exposed to the air they are oxidized and turn brown. They may therefore be used as reducing agents. When treated with strong acids, they behave like aniline and form salts which may be converted into diazonium compounds.

Some of the amino phenol derivatives such as the hydrochloride of para amino phenol,  $(P)C_6H_4 < \begin{smallmatrix} OH \\ NH_2.HCl \end{smallmatrix}$ , are used as photographic developers. Certain derivatives of the amino phenols are manufactured for use also as pharmaceutical preparations and employed medicinally for their beneficial effects. The ethyl ether of para amino phenol,  $(P)C_6H_4 < \begin{smallmatrix} OC_2H_5 \\ NH_2 \end{smallmatrix}$ , is commonly known as *phenetidine*. When phenetidine is heated with acetic acid, it behaves like aniline (see Experiment 69, page 326) and is converted into para acetyl phenetidine,  $(P)C_6H_4 < \begin{smallmatrix} OC_2H_5 \\ NHOCCH_3 \end{smallmatrix}$ , which is commonly called *phenacetin*. This compound is a white crystalline substance which melts at  $135^\circ$ . Phenacetin is used medicinally as an antipyretic.

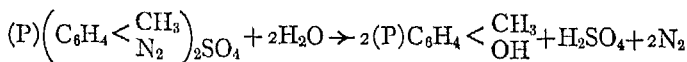
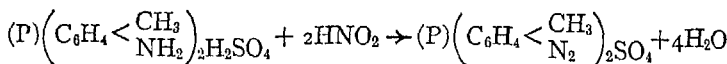
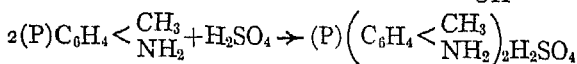
**Cresols**,  $C_6H_4 < \begin{smallmatrix} CH_3 \\ OH \end{smallmatrix}$ . The three isomeric cresols (ortho, meta, and para) are hydroxyl derivatives of toluene. They are present in the distillation products of coal tar and of certain woods such as the beech or pine. As it is very difficult to separate a mixture of the three cresols, they are best obtained in pure condition from the corresponding toluene sulfonic acids:



They may be prepared also from the toluidines,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix}$ , by means of the diazonium compounds. This method of preparing cresols is similar to that used in preparing phenol (see Experiment 76, page 362).

#### EXPERIMENT 79

Preparation of para cresol,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{OH} \end{smallmatrix}$



*Materials*  $\left\{ \begin{array}{l} 30 \text{ grams para toluidine} \\ 18 \text{ cc. concentrated sulfuric acid in } 800 \text{ cc. water} \\ 24 \text{ grams sodium nitrite in } 48 \text{ cc. water} \end{array} \right.$

*Caution!* Do not get the cresol on your hands, as it causes painful burns.

*Procedure.* Place 30 grams of powdered para toluidine in a 2-liter round flask. The dilute sulfuric acid prepared by adding slowly 18 cc. of concentrated sulfuric acid to 800 cc. of water is cooled to the room temperature and added slowly to the para toluidine, and the mixture cooled to room temperature. The para toluidine reacts with the sulfuric acid, forming para toluidine sulfate,

$(\text{P})\left(\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{NH}_2 \end{smallmatrix}\right)_2\text{H}_2\text{SO}_4$ . The sodium nitrite solution, consisting of 24 grams of sodium nitrite dissolved in 48 cc. of water, is now added gradually. If immediate action begins and becomes too vigorous, cool the flask. If the action proceeds very slowly and only a few bubbles of nitrogen escape, warm the flask on a water bath; but should the action again become too energetic, the flask should be cooled. Finally, when the action has slowed down considerably, warm the flask containing the mixture on a water bath heated to about  $40^\circ$

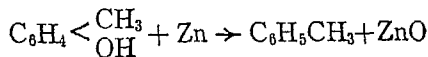
until most of the nitrogen which is evolved has been expelled. The water in the water bath is now heated to the boiling temperature to expel the remaining bubbles of nitrogen and complete the hydrolysis of the diazonium compound. The sodium nitrite solution reacts with the excess of sulfuric acid present, forming nitrous acid. The interaction of the nitrous acid and the sulfate of para toluidine yields the diazonium sulfate of toluene,  $(P)\left(C_6H_4 < \begin{smallmatrix} CH_3 \\ N_2 \end{smallmatrix}\right)_2SO_4$ , which is hydrolyzed to para cresol.

The dark-colored mixture is now steam distilled. The distillation is continued until the yellow oil no longer passes over. The distillate is extracted twice with ether in the following manner: Add about 40 grams of sodium chloride to the distillate, and pour the mixture into a separating funnel. Add about 40 cc. of ether, shake, and separate the top ethereal layer, which is poured into a dry Erlenmeyer flask and stoppered firmly. The bottom layer is again extracted with about 30 cc. of ether, and this second ether extract is poured into the Erlenmeyer flask containing the first ether extract. The combined ether extracts are now dehydrated by treating with about 5 grams of anhydrous sodium sulfate. A stopper is placed firmly in the neck of the flask, which is set aside for several hours. The dried ethereal solution is then filtered into a distilling flask and distilled on a water bath. When no more ether passes over, the water bath is removed and a wire gauze placed under the flask. The para cresol is now distilled and the fraction boiling between  $195^\circ$  to  $204^\circ$  collected. The yellow distillate solidifies on cooling. Calculate the yield and preserve a specimen.

Para cresol is a colorless crystalline substance which melts at  $36^\circ$  and boils at  $202^\circ$ . It is soluble in alcohol and ether.

A. Place a few drops of para cresol in a test tube, and add about 5 cc. of water. Shake the mixture, and to this solution add a few drops of a ferric chloride solution (1 : 10). A blue color is obtained (compare with Experiment 76 B, page 363).

The cresols resemble phenol in their general chemical properties and behavior. They are soluble in alcohol and ether but only slightly soluble in water. When distilled with zinc dust, they are converted to toluene:



The cresols have stronger antiseptic and disinfectant properties than phenol. **Lysol** is a linseed oil soap solution of the three cresols. It is used as an antiseptic wash. The cresols, like phenol, are decomposed somewhat and turn brown when exposed to the air and light. They should be kept in dark-colored bottles.

In the following table are given the formulas of a few phenols and their derivatives. The melting and boiling points of the more important compounds are also included.

PHENOLS

NAME		FORMULA	MELTING POINT, °C.	BOILING POINT, °C
Phenol		$C_6H_5OH$		183
Phenol sulfonic acid		$C_6H_4 \begin{cases} OH \\ SO_2.OH \end{cases}$		
Nitro phenols	Ortho	$C_6H_4 \begin{cases} OH & (1) \\ NO_2 & (2) \end{cases}$	45	
	Meta	$C_6H_4 \begin{cases} OH & (1) \\ NO_2 & (3) \end{cases}$	96	
	Para	$C_6H_4 \begin{cases} OH & (1) \\ NO_2 & (4) \end{cases}$	114	
Potassium nitro phenolate		$C_6H_4 \begin{cases} OK \\ NO_2 \end{cases}$		
Picric acid		$C_6H_2 \begin{cases} OH & (1) \\ (NO_2)_3 & (2, 4, 6) \end{cases}$	122	
Amino phenol		$C_6H_4 \begin{cases} OH \\ NH_2 \end{cases}$		



PHENOLS (*continued*)

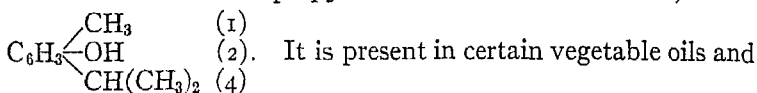
NAME		FORMULA	MELTING POINT, °C	BOILING POINT, °C.
Phenacetin		$(P)C_6H_4 \begin{cases} OC_2H_5 \\ NHOCCH_3 \end{cases}$	135	
Cresols	Ortho	$C_6H_4 \begin{cases} CH_3 & (1) \\ OH & (2) \end{cases}$	31	188
	Meta	$C_6H_4 \begin{cases} CH_3 & (1) \\ OH & (3) \end{cases}$	5	201
	Para	$C_6H_4 \begin{cases} CH_3 & (1) \\ OH & (4) \end{cases}$	36	202
Thymol		$C_6H_3 \begin{cases} CH_3 & (1) \\ OH & (3) \\ CH(CH_3)_2 & (4) \end{cases}$	51	
Dihydroxy phenols	Catechol	$C_6H_4 \begin{cases} OH & (1) \\ OH & (2) \end{cases}$	104	
	Resorcinol	$C_6H_4 \begin{cases} OH & (1) \\ OH & (3) \end{cases}$	110	
	Quinol	$C_6H_4 \begin{cases} OH & (1) \\ OH & (4) \end{cases}$	169	
Pyrogallol		$C_6H_3 \begin{cases} OH & (1) \\ OH & (2) \\ OH & (3) \end{cases}$	115	

Thymol is the isopropyl derivative of meta cresol,

$C_6H_3 \begin{cases} CH_3 & (1) \\ OH & (3) \\ CH(CH_3)_2 & (4) \end{cases}$ . It occurs in certain vegetable oils, such as oil of thyme, from which it is obtained commercially by shaking

these oils with a solution of sodium hydroxide, filtering, and precipitating with hydrogen chloride. It may also be prepared synthetically by reactions which are somewhat complex. It is a colorless crystalline substance which melts at  $51^{\circ}$  and has the agreeable odor of thyme. It has antiseptic properties, but is not poisonous like phenol. Solutions of thymol are used medicinally for their antiseptic properties.

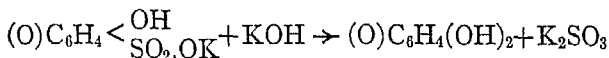
**Carvacrol** is the isopropyl derivative of ortho cresol,



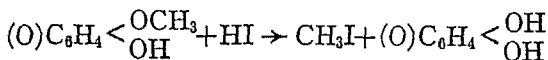
may be prepared synthetically from cymene,  $(P)\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{CH}(\text{CH}_2)_2 \end{smallmatrix}$ , which is converted first into its sulfonic acid derivative and this derivative then converted to the hydroxyl derivative of cymene. Carvacrol is a thick, colorless oil which boils at  $237^{\circ}$ . Unlike its isomer, thymol, it has practically no medicinal value. When treated with a ferric chloride solution, it gives a green color and in this respect differs from thymol.

**Dihydroxy phenols**,  $\text{C}_6\text{H}_4(\text{OH})_2$ . The three dihydroxy phenols are dihydroxy derivatives of benzene.

**Catechol**, (pyrocatechol)  $\text{C}_6\text{H}_4(\text{OH})_2$  (1, 2), occurs in "catechu," which is a substance obtained from certain Indian trees such as the acacia catechu. It may be prepared synthetically from ortho phenol sulfonic acid:

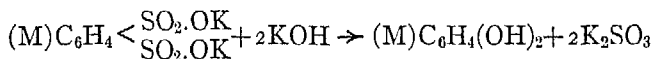


**Guaiacol**, the monomethyl ether of catechol,  $(O)\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OCH}_3 \\ \text{OH} \end{smallmatrix}$ , occurs in the tar obtained from beech wood. Catechol may be prepared most conveniently by heating guaiacol with hydrogen iodide:



Catechol is a crystalline compound which melts at  $104^{\circ}$ , is soluble in water, and gives a characteristic color reaction with ferric chloride.

**Resorcinol**,  $C_6H_4(OH)_2(1, 3)$ , is prepared by fusing meta benzene disulfonic acid with potassium hydroxide:

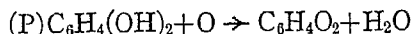


Resorcinol is a crystalline substance which melts at  $110^{\circ}$ , is soluble in water, alcohol, and ether, and gives a color reaction with ferric chloride. When resorcinol is treated with phthalic anhydride, a brown mass is obtained which is the crude, or impure, dye fluorescein. When the crude dye fluorescein is treated with sodium hydroxide and the solution poured into a large volume of water, a beautiful yellowish-green fluorescent color is obtained. Resorcinol is used in large quantities for the preparation of fluorescein, eosin, and certain dyes.

**Quinol**, (hydroquinone)  $C_6H_4(OH)_2(1, 4)$ , occurs as a glucoside in the leaves of the bearberry. It may be made from para amino phenol,  $(P)C_6H_4 < \begin{smallmatrix} OH \\ NH_2 \end{smallmatrix}$ , by means of the diazo reactions, though it is prepared most conveniently by reducing quinone,  $C_6H_4O_2$ , with sulfurous acid:



It is a crystalline compound, soluble in water, and melts at  $169^{\circ}$ . It is oxidized easily to quinone:



Quinol is used as a photographic developer.

#### EXPERIMENT 80

##### Color reactions of dihydroxy phenols, $C_6H_4(OH)_2$

Dissolve about 3 grams of ferric chloride in about 30 cc. of water. This solution of ferric chloride should be used for the following tests:

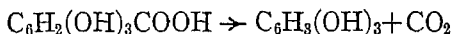
A. Dissolve about 0.5 gram of catechol,  $C_6H_4(OH)_2(1, 2)$  in about 5 cc. of water. Add about 2 cc. of the ferric chloride solution. A green color is obtained. To this mixture add slowly a solution of sodium carbonate (1:10). The green color turns violet and then red on the addition of the sodium carbonate solution.

B. About 0.5 gram of resorcinol,  $C_6H_4(OH)_2(1, 3)$ , is dissolved in about 5 cc. of water. Add about 2 cc. of ferric chloride solution. A dark-violet color is obtained. Add to this mixture a solution of sodium acetate (1:10), and the violet color disappears.

C. Dissolve about 0.5 gram of quinol,  $C_6H_4(OH)_2(1, 4)$ , in about 3 cc. of water. Add about 3 cc. of ferric chloride solution. The dark-green color which is obtained turns yellow.

Pyrogallol, (pyrogallic acid)  $C_6H_3 \begin{matrix} \text{OH} & (1) \\ \text{OH} & (2) \\ \text{OH} & (3) \end{matrix}$ , is prepared by

heating gallic acid,  $C_6H_2 \begin{matrix} (OH)_3(1, 2, 3) \\ COOH(5) \end{matrix}$ :

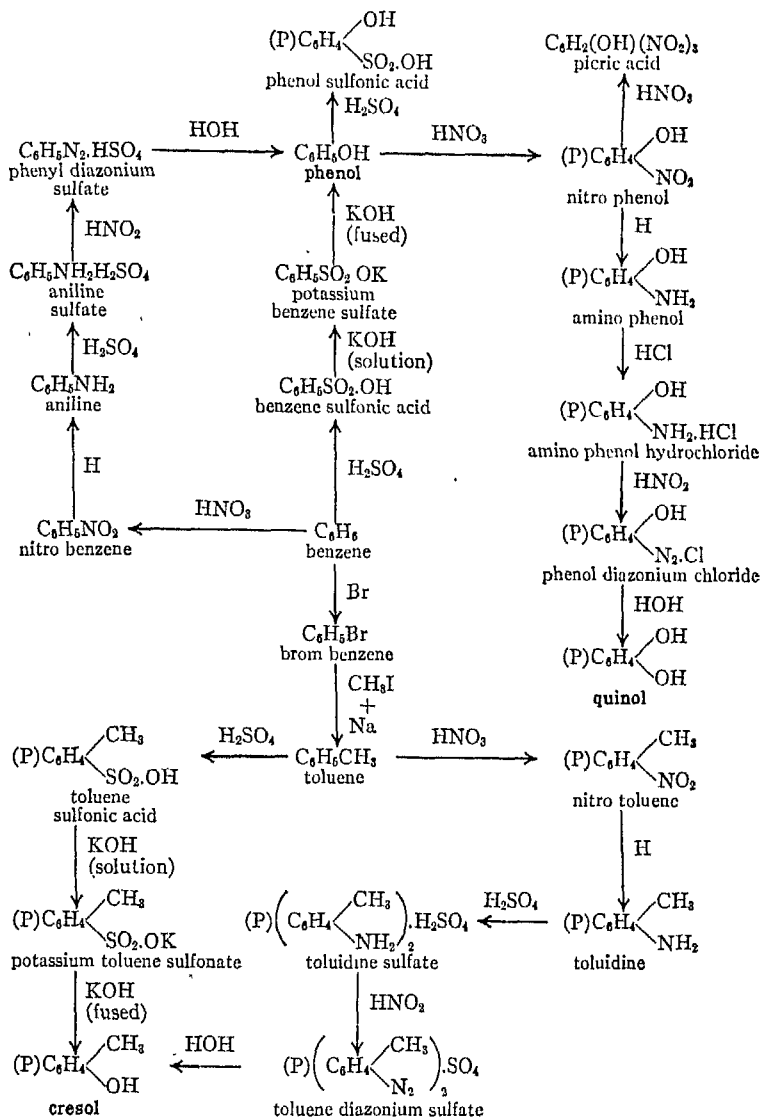


It is a crystalline substance which melts at  $115^\circ$  and is soluble in water. When treated with alkali solutions it dissolves, giving alkaline solutions of pyrogallol, which when exposed to the air absorb oxygen and turn brown. This behavior of pyrogallol is used in gas analysis for the determination of oxygen. Pyrogallol is an active reducing agent and precipitates gold, silver, and mercury from solutions of their salts. It is used in photography as a developer.

The two compounds isomeric with pyrogallol are phloroglucinol,  $C_6H_3(OH)_3(1, 3, 5)$ , and hydroxy quinol,  $C_6H_3(OH)_3(1, 2, 4)$ . Phloroglucinol is a crystalline substance which melts at  $218^\circ$  and gives a violet color with ferric chloride solution. Hydroxyquinol melts at  $140^\circ$  and when treated with a ferric chloride solution gives a brown color.

The general methods used to prepare the phenols are the sulfonic acid and diazo reactions. These reactions are illustrated in the following chart showing the preparation of a few phenols:

## PHENOLS



## QUESTIONS

1. What kind of compounds are phenols?
2. Write outline equations showing two general methods for preparing phenol from benzene.
3. Explain, with equations, the preparation of phenol from aniline.
4. How could you test for phenol?
5. What are some of the characteristic reactions of phenol?
6. In what respect does phenol resemble a tertiary alcohol?
7. Explain, with equations, the preparation of ortho and para nitro phenols. How are these compounds separated?
8. How is the potassium salt of ortho nitro phenol prepared?
9. Write the structural formulas of para phenol sulfonic acid; picric acid; para amino phenol hydrochloride.
10. Explain, with equations, the preparation of para cresol by means of the diazo reaction.
11. For what purposes are the following compounds used. phenol; cresol; ammonium picrate; phenacetin; thymol; resorcinol; quinol; pyrogallol?
12. Write outline equations showing the preparation of para cresol from toluene by means of the sulfonic acid reactions.
13. A compound has the molecular formula  $C_6H_7NO$  and forms salts with both acids and bases. Write a structural formula for this substance.

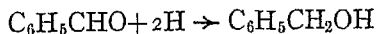
## CHAPTER TWENTY-FOUR

### ALCOHOLS, ETHERS, ALDEHYDES, KETONES, AND QUINONES

#### AROMATIC ALCOHOLS

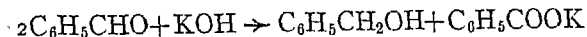
As previously stated, there are two classes of aromatic hydroxyl compounds. Those such as cresol,  $\text{C}_6\text{H}_4\text{CH}_3$ , which have the hydroxyl group in the ring, are known as *phenols*, while those like benzyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ , which have the hydroxyl in the side chain, are called *aromatic alcohols*. The aromatic alcohols resemble the aliphatic alcohols in their general chemical behavior, although they have also the general properties of aromatic compounds. They may be prepared usually by the methods which are used for the preparation of aliphatic alcohols.

**Benzyl alcohol**,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ , is the hydroxyl derivative of toluene. The chemistry of benzyl alcohol illustrates in a general manner the methods of preparation and chemical behavior of aromatic alcohols. Benzyl alcohol may be obtained by reducing benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ :



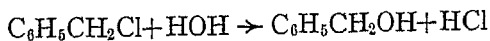
What is formed by the reduction of acetaldehyde?

It is formed also by the interaction of benzaldehyde and a solution of potassium hydroxide:



In this reaction one half of the benzaldehyde is reduced to benzyl alcohol, while the other half is oxidized to benzoic acid, which reacts with the excess of alkali present, forming potassium benzoate,  $\text{C}_6\text{H}_5\text{COOK}$ . This behavior of aromatic aldehydes is quite different from the aliphatic aldehydes, which form resins when treated with alkali solutions.

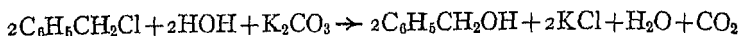
Benzyl alcohol is prepared also by hydrolyzing benzyl chloride:



This reaction is accelerated considerably by hydrolyzing benzyl chloride with an alkaline solution.

### EXPERIMENT 81

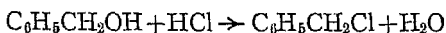
#### Preparation of benzyl alcohol, $C_6H_5CH_2OH$



*Materials* { 27 cc. benzyl chloride  
24 grams of potassium carbonate in 300 cc. of water

*Procedure.* Pour 27 cc. of benzyl chloride into a 500 cc. round flask. Add to this a solution of potassium carbonate prepared by dissolving 24 grams of potassium carbonate in 300 cc. of water. Add a few small pieces of pumice stone (pea size) or a few pieces of broken glass. This is to prevent the solution from bumping when it is heated. The flask is attached to a reflux condenser and boiled gently about 6 hours. The apparatus is now disconnected and the solution allowed to cool to the room temperature. The reaction product is extracted with ether by pouring it into a separating funnel, adding about 50 cc. of ether, and separating the top ethereal layer. The ethereal solution is poured into an Erlenmeyer flask, and to it is added about 4 grams of anhydrous potassium carbonate. The flask should be stoppered firmly and set aside for several hours. The dehydrated ethereal solution is filtered into a distilling flask, which is now attached to a condenser and the ether distilled off on a water bath. When no more ether distills over, the water bath is replaced by a wire gauze, the receiver changed, and the distillation continued. Collect the fraction boiling between  $200^\circ$  and  $210^\circ$ . The boiling point of benzyl alcohol is  $206^\circ$ . Preserve a specimen.

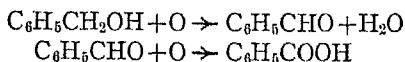
A. Warm about 1 cc. of benzyl alcohol with 1 cc. of concentrated hydrogen chloride. The clear solution becomes turbid, and benzyl chloride separates out:



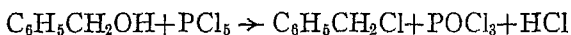
B. Boil about 3 drops of benzyl alcohol with 2 cc. of dilute nitric acid (1:4). The benzyl alcohol is oxidized to benzaldehyde,  $C_6H_5CHO$ , which may be recognized by its odor. Continue to boil the mixture until the odor of benzaldehyde is no longer apparent.



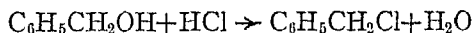
The benzaldehyde is oxidized to benzoic acid,  $C_6H_5COOH$ , which is obtained as white crystals when the solution is cooled in ice water:



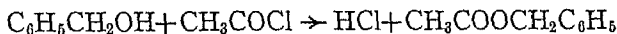
Benzyl alcohol, or phenyl carbinol, is isomeric with the three cresols. It is a colorless liquid which is soluble in alcohol and ether but only slightly soluble in water and has a slight aromatic odor. The benzyl ester of benzoic acid,  $C_6H_5COOCH_2C_6H_5$ , and the benzyl ester of cinnamic acid,  $C_6H_5CH=CHCOOCH_2C_6H_5$ , occur in the balsams of Tolu and Peru, and from these esters benzyl alcohol may be obtained. Benzyl alcohol contains the  $(CH_2OH)$  group and is a primary alcohol. The reactions of benzyl alcohol are analogous to those of the aliphatic primary alcohols. When benzyl alcohol is treated with sodium, hydrogen is evolved, but salts of benzyl alcohol are not obtained, as they are unstable and decomposed by water. When treated with the chlorides of phosphorus, or hydrogen chloride, it forms benzyl chloride:



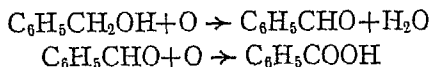
Esters of the aromatic alcohols are obtained readily by treating the alcohols with acids, anhydrides, or acid chlorides. Thus benzyl chloride is formed by the interaction of benzyl alcohol and hydrogen chloride:



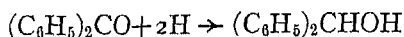
Benzyl acetate,  $CH_3COOCH_2C_6H_5$ , is obtained by treating benzyl alcohol with acetyl chloride:



When oxidized with dilute nitric acid, benzyl alcohol yields benzaldehyde,  $C_6H_5CHO$ , which on further oxidation is converted to benzoic acid,  $C_6H_5COOH$  (Experiment 81 B, above):



**Diphenyl carbinol**,  $(C_6H_5)_2CHOH$ , is an aromatic secondary alcohol. It is prepared by reducing benzophenone, (diphenyl ketone)  $(C_6H_5)_2CO$ :



The method of preparation is similar to that used to obtain the aliphatic secondary alcohols. It is a crystalline substance which melts at  $68^\circ$  and boils at  $298^\circ$ .

**Triphenyl carbinol**,  $(C_6H_5)_3COH$ , is an aromatic tertiary alcohol. It melts at  $159^\circ$  and is obtained by the oxidation of triphenyl methane,  $(C_6H_5)_3CH$ .

**Salicyl alcohol**, (ortho hydroxy benzyl alcohol)

$(O)C_6H_4 < \begin{smallmatrix} OH \\ CH_2OH \end{smallmatrix}$ , is an aromatic phenol alcohol which may be

prepared by the reduction of salicylaldehyde,  $(O)C_6H_4 < \begin{smallmatrix} OH \\ CHO \end{smallmatrix}$ .

It is obtained also from the glucoside salicin, which occurs in the bark of the willow tree. It melts at  $86^\circ$ , is soluble in water, and gives a blue color with ferric chloride.

**Anisyl alcohol**,  $(P)C_6H_4 < \begin{smallmatrix} OCH_3 \\ CH_2OH \end{smallmatrix}$ , is prepared by reducing anisaldehyde,  $(P)C_6H_4 < \begin{smallmatrix} OCH_3 \\ CHO \end{smallmatrix}$ . It is a crystalline substance which melts at  $25^\circ$  and boils at  $258^\circ$ . When oxidized it is converted into anisaldehyde and anisic acid,  $(P)C_6H_4 < \begin{smallmatrix} OCH_3 \\ COOH \end{smallmatrix}$ .

**Cinnamyl alcohol**,  $C_6H_5CH=CHCH_2OH$ , the phenyl derivative of allyl alcohol,  $CH_2=CHCH_2OH$ , is an unsaturated side chain alcohol. It occurs as an ester of cinnamic acid in liquid storax, which is obtained from the sap of a tree found in Asia Minor. It is a crystalline substance which melts at  $33^\circ$  and boils at  $254^\circ$ . It is soluble in water and has the odor of hyacinths. It is reduced to phenyl propyl alcohol,  $C_6H_5CH_2CH_2CH_2OH$ , and when oxidized it is converted into cinnamic aldehyde,  $C_6H_5CH=CHCHO$ , and cinnamic acid,  $C_6H_5CH=CHCOOH$ .

Stronger oxidizing agents convert it into benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ .

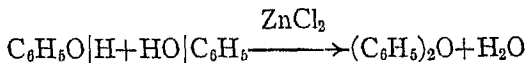
## AROMATIC ALCOHOLS

NAME	FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Benzyl alcohol	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$		206
Diphenyl carbinol	$\begin{matrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{matrix} \text{CHOH}$	68	298
Triphenyl carbinol	$(\text{C}_6\text{H}_5)_3\text{COH}$	159	
Salicyl alcohol	$(\text{O})\text{C}_6\text{H}_4 \begin{matrix} \text{OH} \\ \text{CH}_2\text{OH} \end{matrix}$	86	
Anisyl alcohol	$(\text{P})\text{C}_6\text{H}_4 \begin{matrix} \text{OCH}_3 \\ \text{CH}_2\text{OH} \end{matrix}$	25	258
Cinnamyl alcohol	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$	33	254

## AROMATIC ETHERS

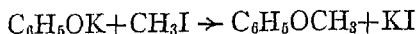
Aromatic ethers are compounds such as diphenyl ether,  $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$ , which contain two aromatic radicals united by one atom of oxygen, or compounds like phenyl methyl ether,  $\text{C}_6\text{H}_5\text{OCH}_3$ , which contain an aromatic and an aliphatic radical.

Diphenyl ether,  $\begin{matrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{matrix} > \text{O}$ , may be prepared by several methods, one of which is by heating phenol with anhydrous zinc chloride:



It is a crystalline substance which melts at  $28^\circ$ , boils at  $252^\circ$ , dissolves in alcohol and ether, and has an odor like that of geraniums.

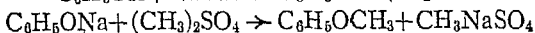
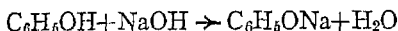
**Anisol**, (phenyl methyl ether)  $C_6H_5OCH_3$ , may be obtained by heating potassium phenolate with methyl iodide:



It is prepared also from phenol by converting it into sodium phenolate,  $C_6H_5ONa$ , which interacts with dimethyl sulfate,  $(CH_3)_2SO_4$ , forming anisol (Ullman's reaction).

## EXPERIMENT 82

### Preparation of anisol, $C_6H_5OCH_3$ (Phenyl methyl ether)



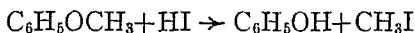
*Materials* { 17 grams of phenol  
Solution of 9 grams sodium hydroxide in 50 cc. water  
28 cc. of dimethyl sulfate  
Ice water

*Caution!* Do not get the phenol on your hands.

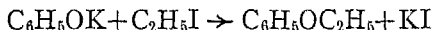
*Procedure.* Pour 50 cc. of water into a 300 cc. flask. Add 9 grams of sodium hydroxide. Shake until dissolved, and cool to room temperature. Add to this mixture 17 grams of phenol. The mixture is now placed in a hood and treated carefully with 28 cc. of dimethyl sulfate. (*Caution!* As the dimethyl sulfate is poisonous, be careful not to breathe the vapors of it.) Place a thermometer in the flask, and endeavor to maintain the temperature of the mixture between  $40^\circ$  and  $50^\circ$ . When the temperature rises above  $50^\circ$ , the flask is immersed temporarily in ice water. The mixture becomes turbid, and in a few minutes an oil is formed which floats upon the surface. The reaction is complete when the mixture ceases to generate heat and it is no longer necessary to cool it in order to keep the temperature below  $50^\circ$ . The excess of dimethyl sulfate may be eliminated by warming the mixture until it boils and shaking the flask frequently. The mixture is now cooled to the room temperature and made slightly alkaline with a dilute solution of sodium hydroxide (1 : 10). The reaction product is extracted with ether by pouring the mixture into a separating funnel, adding about 30 cc. of ether, shaking, and separating the top ethereal layer. The ethereal solution

containing the anisol is poured into an Erlenmeyer flask, treated with about 4 grams of anhydrous potassium carbonate to dehydrate it, and the flask stoppered firmly and set aside for several hours. The dehydrated ethereal solution is then filtered into a dry distilling flask and the ether distilled off on a water bath. The water bath is now replaced by a wire gauze and the anisol distilled. The boiling point of anisol is  $155^{\circ}$ . Preserve a specimen.

Anisol is a colorless liquid which has a very fragrant odor. It is soluble in alcohol and ether and has a specific gravity of 0.991 at  $15^{\circ}$ . The general chemical properties of anisol are similar to those of the aliphatic ethers. It reacts with hydrogen iodide, yielding phenol and methyl iodide :



**Phenetol**, (phenyl ethyl ether)  $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ , may be prepared by the interaction of potassium phenolate and ethyl iodide :



It is a colorless liquid which has an agreeable odor and boils at  $172^{\circ}$ .

There are a number of mixed compounds which contain also, in addition to ether groups, other groups such as alkyl, aldehyde, and hydroxyl. Some of these substances are compounds of considerable importance.

**Guaiacol**, (monomethyl ether of catechol)  $(\text{O})\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \\ \text{OCH}_3 \end{smallmatrix}$ , has been mentioned already as the substance from which catechol,  $(\text{O})\text{C}_6\text{H}_4(\text{OH})_2$ , is prepared. Guaiacol is obtained from guaiacum gum and beech-wood tar and may also be prepared synthetically. It melts at  $28^{\circ}$ , boils at  $205^{\circ}$ , and gives a green color with ferric chloride.

• **Eugenol**,  $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{OH} \\ \text{OCH}_3 \\ \text{CH}_2\text{CH}=\text{CH}_2 \end{smallmatrix}$   $\begin{smallmatrix} (1) \\ (2) \\ (4) \end{smallmatrix}$ , occurs in the oil of cloves

and other essential oils, and is obtained by steam-distilling cloves. Eugenol is a colorless oil which boils at  $247^{\circ}$  and has the odor of

cloves. When oxidized with potassium permanganate it is converted into vanillin.

## AROMATIC ETHERS

NAME	FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Diphenyl ether	$C_6H_5OC_6H_5$	28	252
Anisol	$C_6H_5OCH_3$		155
Phenetol	$C_6H_5OC_2H_5$		172
Guaiacol	$(O)C_6H_4 \begin{cases} OCH_3 \\ OH \end{cases}$	28	205
Eugenol	$C_6H_3 \begin{cases} OH & (1) \\ OCH_3 & (2) \\ CH_2CH=CH_2 & (4) \end{cases}$		247
Vanillin	$C_6H_3 \begin{cases} OH & (4) \\ OCH_3 & (3) \\ CHO & (1) \end{cases}$	81	
Safrol	$C_6H_3 \begin{cases} CH_2CH=CH_2 & (1) \\ O > CH_2 & (3) \\ O & (4) \end{cases}$	8	232
Piperonal	$C_6H_3 \begin{cases} CHO & (1) \\ O > CH_2 & (3) \\ O & (4) \end{cases}$	37	263
Anethol	$(P)C_6H_4 \begin{cases} OCH_3 \\ CH=CHCH_3 \end{cases}$	21	

**Vanillin**,  $C_6H_3(OH)(OCH_3)(CHO)(4, 3, 1)$ , is the principal constituent of vanilla, which is the alcoholic extract of vanilla beans. It is prepared commercially by oxidizing eugenol. Vanillin is a crystalline substance which melts at  $81^\circ$ . It has the

odor and taste of vanilla, and gives a blue color with ferric chloride. Vanillin is manufactured commercially for use in flavoring extracts and perfumery.

**Safrol**,  $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{CH}_2\text{CH}=\text{CH}_2 & (1) \\ \diagup \text{O} \diagdown & (3) \\ \text{O} & (4) \end{smallmatrix} > \text{CH}_2$ , is the principal constituent

of oil of sassafras. It melts at  $8^\circ$  and boils at  $232^\circ$ .

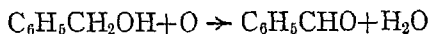
**Piperonal**,  $\text{C}_6\text{H}_3 \begin{smallmatrix} \text{CHO} & (1) \\ \diagup \text{O} \diagdown & (3) \\ \text{O} & (4) \end{smallmatrix} > \text{CH}_2$ , is obtained by oxidizing safrol.

It melts at  $37^\circ$  and boils at  $263^\circ$ . Piperonal has the odor of heliotrope and is used in perfumery under the name of *heliotropin*.

**Anethol**,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OCH}_3 \\ \text{CH}=\text{CHCH}_3 \end{smallmatrix}$ , is the chief constituent of oil of aniseed. It is a crystalline substance which melts at  $21^\circ$  and when oxidized with a mixture of potassium dichromate and sulfuric acid is converted into anisaldehyde,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OCH}_3 \\ \text{CHO} \end{smallmatrix}$ .

### AROMATIC ALDEHYDES

The aromatic aldehydes are aromatic compounds which contain the aldehyde group (CHO). They are obtained usually by reactions similar to those used in preparing the aliphatic aldehydes. Thus, when benzyl alcohol,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ , is oxidized, the primary alcohol group ( $\text{CH}_2\text{OH}$ ) is converted into the aldehyde group (CHO) and benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , is obtained (see Experiment 21, page 101):



The aldehyde group (CHO) may be introduced into the ring, forming compounds such as benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , and the <sup>\*</sup>toluic aldehydes,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{CHO} \end{smallmatrix}$ , or it may enter the side chain, giving compounds like phenyl acetaldehyde,  $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ . Compounds containing the aldehyde group in the side chain

resemble the aliphatic aldehydes very closely in their chemical behavior and are not substances of special importance. Many of the aromatic aldehydes which contain the aldehyde group united directly to the ring are compounds of considerable importance, and although they resemble the aliphatic aldehydes in their general chemical behavior, yet in certain respects they are quite different. Reactions showing the general methods of preparation and behavior of benzaldehyde illustrate in a general manner the chemistry of this class of compounds.

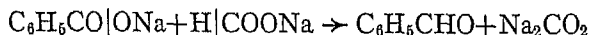
**Benzaldehyde**, (oil of bitter almonds)  $C_6H_5CHO$ , occurs in the glucoside amygdalin,  $C_{20}H_{27}NO_{11}$ , which is obtained from bitter almonds and the kernels of various fruits such as peaches and cherries. Amygdalin is hydrolyzed in the presence of the enzyme emulsin, which occurs with it in the plants yielding benzaldehyde, hydrogen cyanide, and glucose:



Benzaldehyde may be prepared by oxidizing the primary alcohol, benzyl alcohol, with nitric acid:

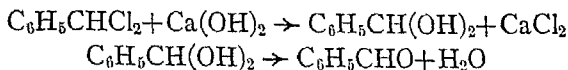


This is a general method which is used to prepare aldehydes. Benzaldehyde is obtained also by another general method, which is that of distilling a mixture of calcium formate,  $(HCOO)_2Ca$ , and the calcium salt of another acid containing the desired radical. Thus the interaction of calcium formate and calcium benzoate,  $(C_6H_5COO)_2Ca$ , yields benzaldehyde. This reaction may be understood more clearly, perhaps, if we unite the formulas of the sodium salts instead of the calcium salts:

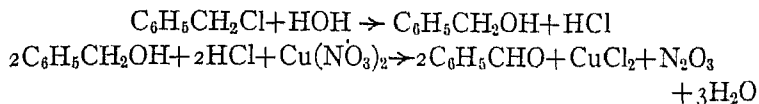


Benzaldehyde is prepared conveniently by hydrolyzing benzal chloride,  $C_6H_5CHCl_2$ , with a solution of calcium hydroxide. The unstable compound  $C_6H_5CH(OH)_2$ , which is probably formed, decomposes into benzaldehyde and water:



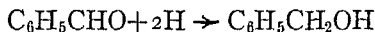


Benzaldehyde is prepared commercially by boiling benzyl chloride,  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ , with an aqueous solution of copper nitrate. In this method the benzyl chloride is probably hydrolyzed to benzyl alcohol, which is then oxidized to benzaldehyde by the copper nitrate:



Benzaldehyde is a colorless oil which boils at  $179^\circ$  and has a specific gravity of 1.05 at  $15^\circ$ . It has the pleasant odor of bitter almonds, distills with steam, and is soluble in alcohol and ether but only slightly soluble in water. It is employed for use as a flavoring material and in the manufacture of dyes.

When benzaldehyde is treated with certain substances, it reacts like the aliphatic aldehydes. It is oxidized easily, yielding benzoic acid, and when reduced it is converted into benzyl alcohol:

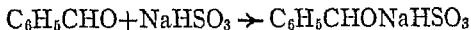


When benzaldehyde is treated with phosphorus pentachloride, it behaves like acetaldehyde and the atom of oxygen is replaced by two atoms of chlorine, yielding benzal chloride,  $\text{C}_6\text{H}_5\text{CHCl}_2$  (see Acetaldehyde, page 100). Benzaldehyde reacts with sodium hydrogen sulfite, forming a crystalline addition product,  $\text{C}_6\text{H}_5\text{CHO} \cdot \text{NaHSO}_3$ , and with hydrogen cyanide, giving an aromatic hydroxy cyanide,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CN}$ .

#### EXPERIMENT 83

##### Reactions of benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$

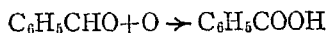
##### • A. Sodium hydrogen sulfite addition product of benzaldehyde



Treat about 20 grams of sodium hydrogen sulfite with an amount of water just sufficient to dissolve it. Stir, and filter the solution.

To this solution add about 4 cc. of benzaldehyde. The beaker containing the mixture is placed in ice water and stirred constantly for a few minutes. Crystals of benzaldehyde sodium hydrogen sulfite,  $C_6H_5CHO \cdot NaHSO_3$ , separate out. Filter, and dry the crystals on filter paper.

### B. Oxidation of benzaldehyde to benzoic acid

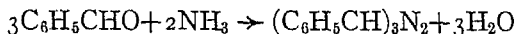


Place a few drops of benzaldehyde on a watch glass and allow the liquid to stand exposed to the air for some time. It is gradually oxidized to a white solid, which is benzoic acid,  $C_6H_5COOH$ .

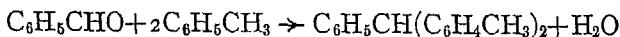
Although benzaldehyde reacts with various substances, giving reactions similar to those of the aliphatic aldehydes, it differs from the aliphatic aldehydes in certain respects. It does not reduce Fehling's solution or undergo polymerization. When treated with alkalis the aliphatic aldehydes yield resins, while benzaldehyde is converted into benzyl alcohol and potassium benzoate,  $C_6H_5COOK$ :



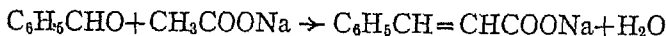
When treated with ammonia, benzaldehyde does not form an addition product but yields hydrobenzamide,  $(C_6H_5CH)_3N_2$ :



Benzaldehyde, like other aromatic aldehydes, reacts with various aliphatic and aromatic compounds, forming condensation products. Thus, when benzaldehyde is treated with toluene under the proper conditions, the two compounds unite, with the elimination of water, and a condensation product is obtained which is a derivative of triphenyl methane:

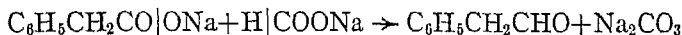


When treated with sodium acetate, benzaldehyde yields a condensation product which is the sodium salt of cinnamic acid,  $C_6H_5CH=CHCOONa$ :



**Toluic aldehydes**,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_3 \\ \text{CHO} \end{smallmatrix}$ , may be obtained by general reactions similar to those used in preparing aldehyde. They resemble benzaldehyde in their general properties. Ortho and meta toluic aldehydes are liquids which have an odor resembling that of benzaldehyde. The boiling point of the ortho compound is  $200^\circ$ , while the meta boils at  $199^\circ$ . Para toluic aldehyde is a liquid which boils at  $204^\circ$  and has an odor like that of pepper.

Compounds such as phenyl acetaldehyde,  $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ , which contain the aldehyde group in the side chain, may be prepared by distilling a mixture of calcium formate and the calcium salt of the acid containing the radical desired. Thus phenyl acetaldehyde may be obtained by the interaction of calcium formate and the calcium salt of phenyl acetic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ . Writing the formulas of the sodium salts instead of the calcium salts, the reaction is:

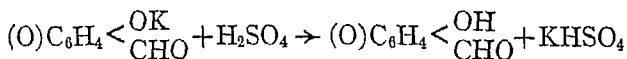
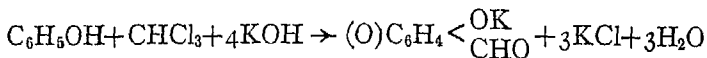


Phenyl acetaldehyde is a liquid which boils at  $206^\circ$ . It is isomeric with the three toluic aldehydes.

**Cinnamic aldehyde**,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ , is the principal constituent of oil of cinnamon. It occurs in other essential oils, such as oil of cassia. It may be obtained from these essential oils by treating them with sodium hydrogen sulfite. The sodium hydrogen sulfite addition product of cinnamic aldehyde is rather insoluble and may be separated from the other constituents present in the essential oils. Cinnamic aldehyde is obtained by treating the addition product with a solution of sodium carbonate and distilling. This is a general method for separating aldehydes from the essential oils in which they occur naturally. Cinnamic aldehyde is an unsaturated side-chain aldehyde and may be prepared by oxidizing cinnamyl alcohol,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$ , or by distilling a mixture of the calcium salts of cinnamic and formic acids. It is a colorless liquid which has an odor like that

of cinnamon and boils at  $247^{\circ}$ . It is soluble in alcohol and ether and when oxidized is converted into cinnamic acid.

**Substituted aromatic aldehydes.** **Salicylic aldehyde**, (ortho hydroxy benzaldehyde)  $(O)C_6H_4 < \begin{smallmatrix} CHO \\ OH \end{smallmatrix}$ , occurs naturally in certain volatile oils and may be obtained by oxidizing saligenin with chromic acid. Saligenin is a glucoside which occurs in willow bark. Salicylic aldehyde may be obtained by oxidizing salicyl alcohol,  $(O)C_6H_4 < \begin{smallmatrix} CH_2OH \\ OH \end{smallmatrix}$ , but it is usually prepared by Reimer's reaction. The process consists of heating an alkaline solution of phenol with chloroform, after which dilute sulfuric acid is added and the mixture steam distilled:



Both the ortho and para salicylic aldehydes are obtained by the reactions above, but only the ortho distills with steam and thus the mixture is separated easily.

Salicylic aldehyde is a colorless fragrant oil which boils at  $196^{\circ}$ . It is fairly soluble in water and gives a violet color with ferric chloride. When treated with nitric acid it is oxidized readily to salicylic acid,  $(O)C_6H_4 < \begin{smallmatrix} OH \\ COOH \end{smallmatrix}$ .

**Anisaldehyde**,  $(P)C_6H_4 < \begin{smallmatrix} OCH_3 \\ CHO \end{smallmatrix}$ , is the methyl ether of para hydroxy benzaldehyde,  $(P)C_6H_4 < \begin{smallmatrix} OH \\ CHO \end{smallmatrix}$ . It is prepared by oxidizing anethol,  $(P)C_6H_4 < \begin{smallmatrix} OCH_3 \\ CH=CHCH_3 \end{smallmatrix}$ , which is the chief constituent of aniseed oil. Anisaldehyde has a pleasant aromatic odor and boils at  $248^{\circ}$ . It is used in the preparation of perfumes.

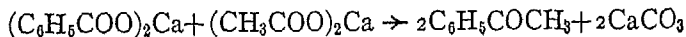
## AROMATIC ALDEHYDES

NAME	FORMULA	BOILING POINT, °C.
Benzaldehyde	$C_6H_5CHO$	179
Toluic aldehyde	$C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown CHO \end{matrix}$	
Phenyl acetaldehyde	$C_6H_5CH_2CHO$	206
Cinnamic aldehyde	$C_6H_5CH=CHCHO$	247
Salicylic aldehyde	$(O)C_6H_4 \begin{matrix} \diagup OH \\ \diagdown CHO \end{matrix}$	196
Anisaldehyde	$(P)C_6H_4 \begin{matrix} \diagup OCH_3 \\ \diagdown CHO \end{matrix}$	248

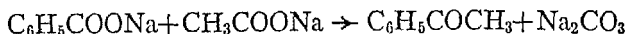
## AROMATIC KETONES

Aromatic ketones contain the carbonyl group (CO) united to two aromatic radicals as in benzophenone,  $\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > CO$ , or united to an aromatic and an aliphatic radical as in acetophenone,  $\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} > CO$ .

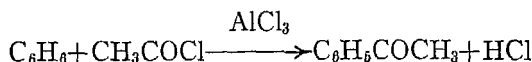
**Acetophenone**, (phenyl methyl ketone)  $C_6H_5COCH_3$ , is the simplest of the aromatic ketones. Reactions showing the methods of preparation and behavior of acetophenone illustrate in a general manner the chemistry of this class of compounds. Acetophenone may be obtained by the general methods which are used for the preparation of aromatic ketones. It is prepared by distilling a mixture of the calcium salts of benzoic and acetic acids:



If we write the formulas of the sodium salts instead of the calcium salts, the reaction is :



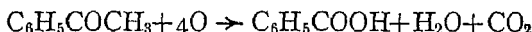
Acetophenone is prepared most conveniently by treating benzene with acetyl chloride in the presence of anhydrous aluminium chloride (Friedel and Crafts' reaction, page 300) :



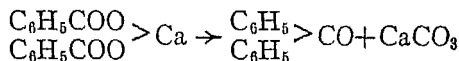
Acetophenone is a crystalline substance which has a sweet odor. It melts at  $20^\circ$  and boils at  $202^\circ$ . It is used medicinally as a hypnotic and is called *hypnone*. The behavior of acetophenone is quite similar to that of the aliphatic ketones such as acetone. When reduced it is converted into the secondary alcohol phenyl methyl carbinol,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$  :



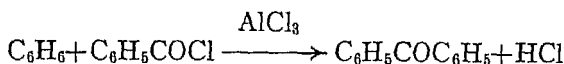
It does not form an addition product with sodium hydrogen sulfite, but when oxidized it is converted into benzoic acid :



**Benzophenone**, (diphenyl ketone)  $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ , may be obtained by distilling calcium benzoate :



It is prepared most conveniently by treating benzene with benzoyl chloride,  $\text{C}_6\text{H}_5\text{COCl}$ , in the presence of aluminium chloride (Friedel and Crafts' reaction) :

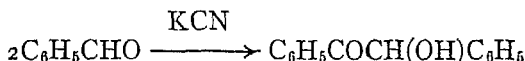


Benzophenone is a fragrant crystalline compound which melts at  $48^\circ$  and boils at  $306^\circ$ . The reactions of benzophenone are similar to those of acetophenone. When reduced with an alcoholic solution of potassium hydroxide and zinc dust it is converted

into diphenyl carbinol,  $(C_6H_5)_2CHOH$ . When heated with hydriodic acid it is reduced to diphenyl methane,  $C_6H_5CH_2C_6H_5$ .

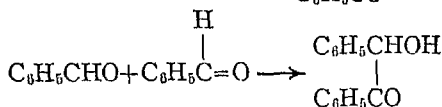
**Benzoin**,  $\begin{array}{c} C_6H_5CHOH \\ | \\ C_6H_5CO \end{array}$ , is an aromatic ketone alcohol which is

prepared from benzaldehyde by the condensation reaction. When an alcoholic solution of benzaldehyde is heated in the presence of potassium cyanide, two molecules of benzaldehyde react to form benzoin:



#### EXPERIMENT 84

**Preparation of benzoin**,  $\begin{array}{c} C_6H_5CHOH \\ | \\ C_6H_5CO \end{array}$



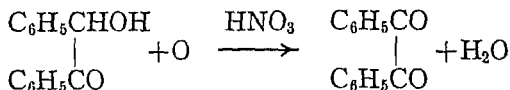
*Materials*  $\left\{ \begin{array}{l} 10 \text{ cc. benzaldehyde} \\ \text{Solution of 2 grams potassium cyanide in 10 cc. water} \\ 20 \text{ cc. of 95 per cent ethyl alcohol} \end{array} \right.$

*Procedure.* Pour 10 cc. of benzaldehyde into a 200 cc. round flask. Add to this 20 cc. of 95 per cent ethyl alcohol. To this mixture is added a solution of potassium cyanide prepared by dissolving 2 grams of potassium cyanide in 10 cc. of water. Connect the flask to a reflux condenser and heat on a water bath about 1 hour. The apparatus is now disconnected and the hot reaction product poured into a beaker. When allowed to cool, the benzoin crystallizes. The product is washed with about 3 cc. of ethyl alcohol, and the benzoin recrystallized by treating it with a sufficient amount of hot ethyl alcohol to dissolve it and allowing it to crystallize. Filter, and dry on layers of filter paper. The melting point is  $137^\circ$ . Preserve a specimen and calculate the yield.

Benzoin is a crystalline compound which is soluble in alcohol and ether but only slightly soluble in water. When ben-

zoin is reduced under the proper conditions, it is converted into benzyl phenyl ketone,  $C_6H_5CH_2COC_6H_5$ , hydrobenzoin,  $C_6H_5CHOH.CHOHC_6H_5$ , or dibenzyl,  $C_6H_5CH_2.CH_2C_6H_5$ .

**Benzil**,  $C_6H_5CO.COC_6H_5$ . When benzoin is heated with concentrated nitric acid, it is oxidized to benzil,  $C_6H_5CO.COC_6H_5$ , which is a diketone:



Benzil is a yellow crystalline substance which melts at  $95^\circ$ .

#### AROMATIC KETONES

NAME	FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Acetophenone	$\begin{array}{c} C_6H_5 \\ \diagup \\ CH_3 \end{array} CO$	20	202
Benzophenone	$\begin{array}{c} C_6H_5 \\ \diagup \\ C_6H_5 \end{array} CO$	48	306
Benzoin	$\begin{array}{c} C_6H_5CHOH \\   \\ C_6H_5CO \end{array}$	137	
Benzil	$\begin{array}{c} C_6H_5CO \\   \\ C_6H_5CO \end{array}$	95	

#### QUINONES

Quinones are compounds which are derived from the aromatic hydrocarbons or their derivatives by replacing two hydrogen atoms by two atoms of oxygen. Thus, if two hydrogen atoms in benzene are substituted by two atoms of oxygen, we obtain the

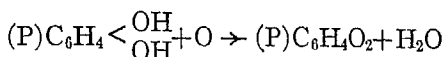


compound quinone, which is the simplest member of the group of compounds known as quinones :

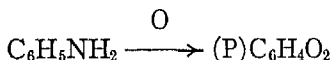


The two oxygen atoms may be introduced into the ortho or para positions, forming ortho or para quinones. Meta quinones have never been prepared. Ortho quinones are not compounds of special importance; the para quinones, however, have been studied considerably.

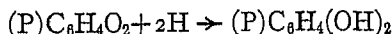
**Quinone**, (P) $\text{C}_6\text{H}_4\text{O}_2$ , is known also as *benzoquinone*, which indicates that it is derived from benzene. It may be obtained by oxidizing quinol, (P) $\text{C}_6\text{H}_4(\text{OH})_2$ , under suitable conditions :



Quinone may be obtained also by oxidizing other para compounds, such as sulfanilic acid, (P) $\text{C}_6\text{H}_4 < \begin{array}{c} \text{NH}_2 \\ \text{SO}_2.\text{OH} \end{array}$ , and para phenol sulfonic acid, (P) $\text{C}_6\text{H}_4 < \begin{array}{c} \text{OH} \\ \text{SO}_2.\text{OH} \end{array}$ . It is prepared most conveniently by oxidizing aniline with a mixture of potassium dichromate and sulfuric acid, extracting the product with ether, separating, and distilling off the excess of ether. In this reaction, which is somewhat complex, the amino group in aniline and the hydrogen atom in the para position to it are each replaced by an atom of oxygen :



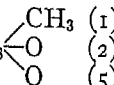
Quinone is a yellow crystalline substance which melts at  $116^\circ$ , sublimes, distils with steam, and has a peculiar irritating odor. It is soluble in alcohol and ether, and when reduced it is converted into quinol (hydroquinone) :



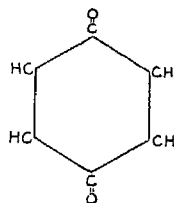


Various formulas representing the structure of quinone have been suggested. Researches which have been carried out lead to the conclusion that quinone is represented in the most satisfactory manner by the formula shown in Figure 37.

Other quinones have properties very similar to

quinone. **Toluquinone**,  $\text{C}_6\text{H}_5$  , is the

quinone derivative of toluene. It is a yellow crystalline substance which melts at  $67^\circ$  and has an odor similar to that of quinone.



Quinone  
Figure 37

In the chart on the opposite page are given outline reactions showing the preparation of a few aromatic alcohols, ethers, aldehydes, ketones, and quinones from benzene.

### QUESTIONS

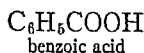
1. What kind of compounds are aromatic alcohols?
2. Explain, with equations, how benzyl alcohol is prepared in the laboratory.
3. Give another name for benzyl alcohol.
4. What compound is obtained by treating benzyl alcohol with hydrogen chloride?  
With acetyl chloride? With oxygen?
5. What kind of compounds are aromatic ethers?
6. Explain, with equations, the laboratory preparation of anisol.
7. Write equations showing the preparation of phenetol from phenol.
8. What kind of compounds are aromatic aldehydes?
9. State one of the methods by which benzaldehyde is obtained from benzyl alcohol.
10. Explain how the sodium hydrogen sulfite addition product of benzaldehyde is prepared.
11. What compound is obtained by the reduction of benzaldehyde? By the oxidation?
12. Write the structural formulas of the following compounds: ortho toluic aldehyde; phenyl acetaldehyde; cinnamic aldehyde; salicylic aldehyde.
13. What kind of compounds are aromatic ketones?
14. Write equations showing the general methods which are used to prepare aromatic ketones.
15. Write the structural formulas of acetophenone and benzophenone. What substances are formed by the reduction of these compounds?
16. Explain, with equations, how benzoin is prepared in the laboratory.
17. What kind of compounds are quinones?

18. Write an equation showing the preparation of quinone from quinol.
19. How is quinone usually prepared in the laboratory?
20. Write the structural formula of quinone.
21. What compound is obtained by the reduction of quinone?
22. Write the following outline reactions, showing all intermediate products:
  - a. benzene  $\rightarrow$  aniline  $\rightarrow$  quinone.
  - b. benzene  $\rightarrow$  phenol  $\rightarrow$  phenetol.
  - c. benzene  $\rightarrow$  benzyl alcohol  $\rightarrow$  benzoic acid.

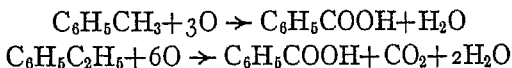
## CHAPTER TWENTY-FIVE

### AROMATIC CARBOXYL ACIDS

THE aromatic carboxyl acids are aromatic compounds containing the carboxyl group ( $\text{COOH}$ ). These compounds are derived from the aromatic hydrocarbons by replacing one or more hydrogen atoms by the carboxyl group. Thus, if one hydrogen atom in benzene is replaced by the carboxyl group, the resulting compound is the monocarboxyl derivative of benzene, which is called *benzoic acid*:



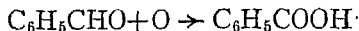
The carboxyl group may be introduced into the ring, yielding compounds such as benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , toluic acid,  $\text{C}_6\text{H}_4<\overset{\text{CH}_3}{\text{COOH}}$ , and phthalic acid,  $\text{C}_6\text{H}_4(\text{COOH})_2$ ; or it may enter the side chain, giving compounds like phenyl acetic acid,  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ . Many of the aromatic carboxyl acids occur naturally as the free acid or as esters in balsams, resins, and the oils obtained from plants. They may be prepared synthetically by the general methods that are used to prepare the aliphatic carboxyl acids, which are oxidation of alcohols and aldehydes, and the hydrolysis of nitriles and esters. They may be obtained also by the oxidation of a side chain radical. Thus benzoic acid may be prepared by the oxidation of toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ , or ethyl benzene,  $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ :



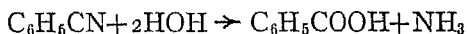
This method cannot be used for the preparation of aliphatic carboxyl acids or of aromatic acids containing the carboxyl group in the side chain and is useful only for the preparation of aromatic acids containing the carboxyl group united directly to the ring.

**Benzoic acid**, (phenyl formic acid)  $\text{C}_6\text{H}_5\text{COOH}$ , the simplest of the aromatic carboxyl acids, occurs in gum benzoin, the balsams

of Peru and Tolu, and certain resins. It is present also as benzoyl amino acetic acid, (benzoyl glycine)  $C_6H_5CONHCH_2COOH$ , in the urine of herbivorous animals. It is prepared commercially by subliming gum benzoin, and also from toluene, which is chlorinated to benzyl chloride,  $C_6H_5CH_2Cl$ , and this substance is then oxidized by dilute nitric acid to benzoic acid. It may be prepared in the laboratory by the oxidation of benzyl alcohol or benzaldehyde (Experiments 80 *B*, page 376, and 81 *B*, page 380).

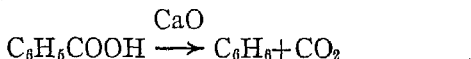


It is obtained also by hydrolyzing phenyl cyanide,  $C_6H_5CN$ :



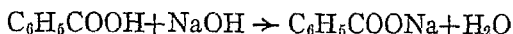
Benzoic acid is a crystalline substance which melts at  $121.5^\circ$  and boils at  $249^\circ$ . It sublimes readily, distils with steam, is soluble in alcohol, ether, and hot water but is difficultly soluble in cold water. It is a strong antiseptic.

When heated with lime, benzoic acid is decomposed, yielding benzene and carbon dioxide:



The aromatic carboxyl acids yield derivatives such as salts, esters, acid chlorides, acid amides, and acid anhydrides corresponding to the aliphatic carboxyl acids, and are prepared usually by reactions similar to those employed for the preparation of the aliphatic compounds.

Salts such as sodium benzoate,  $C_6H_5COONa$ , are prepared by treating the carboxyl acids with hydroxides or carbonates:

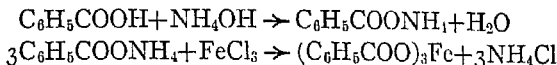


The alkali salts of the aromatic carboxyl acids are soluble in water, and the acids may be obtained from them by treating with inorganic acids such as hydrogen chloride:



Sodium benzoate,  $\text{C}_6\text{H}_5\text{COONa}$ , is used considerably as a food preservative.

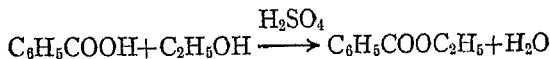
## EXPERIMENT 85

**Ferric benzoate,  $(\text{C}_6\text{H}_5\text{COO})_3\text{Fe}$** 

Treat about 0.2 gram of benzoic acid with a sufficient amount of hot water to dissolve it. Test the solution with litmus paper. Does it have an acid reaction? Add to the aqueous solution of benzoic acid a dilute solution of ammonia (1:10) until the mixture has a neutral or slightly alkaline reaction. Boil off the excess of ammonia, and add a solution of ferric chloride (1:10). A dark-yellow precipitate of ferric benzoate is obtained.

Esters of the aromatic carboxyl acids are prepared by treating the acids with alcohols in the presence of a dehydrating agent such as hydrogen chloride or sulfuric acid. Thus **methyl benzoate**,  $\text{C}_6\text{H}_5\text{COOCH}_3$ , is prepared by saturating a mixture of benzoic acid and methyl alcohol with hydrogen chloride gas. The mixture is heated about 3 hours on a water bath, after which it is distilled. Methyl benzoate is a fragrant oil which boils at  $199^\circ$ . **Ethyl benzoate**,  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ , may be obtained in a similar manner, though it is prepared more conveniently by the interaction of benzoic acid and ethyl alcohol in the presence of sulfuric acid. This method of preparation is similar to that used for the preparation of ethyl acetate (see Experiment 28, page 132).

## EXPERIMENT 86

**Preparation of ethyl benzoate,  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$** 

• *Materials*  $\left\{ \begin{array}{l} 15 \text{ grams benzoic acid} \\ 45 \text{ cc. absolute alcohol} \\ 4 \text{ cc. concentrated sulfuric acid} \end{array} \right.$

*Procedure.* Place 15 grams of powdered benzoic acid in a dry 200 cc. round flask. Add 45 cc. of absolute ethyl alcohol. The

flask containing the mixture is shaken a few minutes until most of the benzoic acid is dissolved. Now add 4 cc. of concentrated sulfuric acid and shake the flask a few times. The flask is now connected to a reflux condenser and heated on a boiling water bath about 2 hours. The apparatus is disconnected and the reaction product poured into a dry 150 cc. distilling flask, which is now connected to a condenser. The mixture is distilled on a water bath to eliminate the excess of alcohol. When no more alcohol passes over, disconnect the apparatus and pour the reaction product into a beaker containing about 150 cc. of water. Stir the mixture, and add a concentrated solution of sodium carbonate to neutralize the acid present. The carbonate solution is added until no more bubbles of carbon dioxide are evolved and the solution no longer shows a distinct acid reaction with litmus paper. The mixture is extracted twice with ether in the following manner: Add about 40 cc. of ether, pour the mixture into a separating funnel, shake, and separate the top ethereal layer, which is poured into a dry Erlenmeyer flask. The bottom layer is again treated with about 20 cc. of ether, the mixture shaken and separated, and the top layer poured into the Erlenmeyer flask containing the first ether extract. Add about 3 grams of anhydrous potassium carbonate, place a stopper in the neck of the flask, and set the flask aside for several hours to dehydrate the ethereal solution. The mixture is now filtered into a dry distilling flask and the ether distilled off on a water bath. The water bath is replaced by a wire gauze and the ester distilled. The boiling point of ethyl benzoate is  $211^{\circ}$ . Preserve a specimen and calculate the yield.

Ethyl benzoate is an oil which has a pleasant aromatic odor. Both methyl and ethyl benzoates are decomposed by boiling with an alcoholic solution of sodium hydroxide (see Experiment 29, page 137).

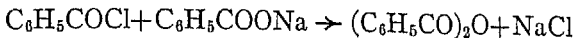
**Benzoyl chloride**,  $C_6H_5COCl$ , is obtained by treating benzoic acid with phosphorus pentachloride and distilling the mixture:



It is a colorless liquid which boils at  $198^{\circ}$ , fumes in the air, and has an irritating odor. When treated with cold water it is gradually converted to benzoic acid.

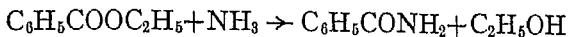


**Benzoic anhydride**,  $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ , is prepared by the interaction of benzoyl chloride and sodium benzoate (see Experiment 31, page 144):



It is a crystalline compound which melts at  $42^\circ$  and resembles acetic anhydride in its behavior. When boiled with water it is converted to benzoic acid.

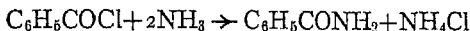
**Benzamide**,  $\text{C}_6\text{H}_5\text{CONH}_2$ , is obtained by treating ethyl benzoate with ammonia (Experiment 32, page 147):



It is prepared conveniently in the laboratory by the interaction of benzoyl chloride and ammonia.

#### EXPERIMENT 87

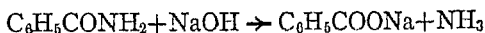
##### Preparation of benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$



*Materials*  $\left\{ \begin{array}{l} 4 \text{ cc. benzoyl chloride} \\ 20 \text{ cc. concentrated ammonia} \end{array} \right.$

*Procedure.* Measure out 4 cc. of benzoyl chloride in a dry graduated cylinder, and pour it into a dry dropping funnel which is attached to an iron stand. Pour 20 cc. of concentrated ammonia into a beaker, and place it under the dropping funnel containing the benzoyl chloride. Allow the benzoyl chloride to drop slowly into the ammonia, which is stirred frequently. The benzamide separates out as a white precipitate. When all the benzoyl chloride has been added, treat the reaction product with 30 cc. of water. Cool, stir, and filter. Wash the benzamide with a small amount of cold water. It may be recrystallized by dissolving in hot water and allowing the solution to crystallize. The melting point is  $130^\circ$ .

- A. Place about 0.5 gram of benzamide in a test tube, add about 3 cc. of sodium hydroxide solution (1:10), and boil. Ammonia is evolved (see Experiment 32 A, page 148):



## AROMATIC CARBOXYL ACIDS AND DERIVATIVES

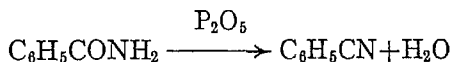
NAME	FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Benzoic acid	$C_6H_5COOH$	121.5	249
Ethyl benzoate	$C_6H_5COOC_2H_5$		211
Benzoyl chloride	$C_6H_5COCl$		198
Benzamide	$C_6H_5CONH_2$	130	
Toluic acid	$C_6H_4 \begin{matrix} \nearrow CH_3 \\ \searrow COOH \end{matrix}$		
Phenyl acetic acid	$C_6H_5CH_2COOH$	76	
Cinnamic acid	$C_6H_5CH=CHCOOH$	133	
Mandelic acid	$C_6H_5CH(OH)COOH$	118	
Sulfo benzoic acid	$C_6H_4 \begin{matrix} \nearrow COOH \\ \searrow SO_2.OH \end{matrix}$		
Saccharin	$(O)C_6H_4 \begin{matrix} \nearrow CO \\ \searrow SO_2 \end{matrix} NH$	224	
Nitro benzoic acid	$C_6H_4 \begin{matrix} \nearrow NO_2 \\ \searrow COOH \end{matrix}$		
Amino benzoic acid	$C_6H_4 \begin{matrix} \nearrow NH_2 \\ \searrow COOH \end{matrix}$		
Salicylic acid	$(O)C_6H_4 \begin{matrix} \nearrow OH \\ \searrow COOH \end{matrix}$	156	

AROMATIC CARBOXYL ACIDS AND DERIVATIVES (*continued*)

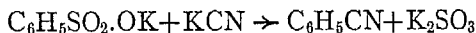
NAME	FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Methyl salicylate	$(\text{O})\text{C}_6\text{H}_4 \begin{cases} \text{OH} \\ \text{COOCH}_3 \end{cases}$		224
Salol	$(\text{O})\text{C}_6\text{H}_4 \begin{cases} \text{OH} \\ \text{COOC}_6\text{H}_5 \end{cases}$	42	
Aspirin	$\text{C}_6\text{H}_4 \begin{cases} \text{OOCCH}_3 \\ \text{COOH} \end{cases}$	135	
Gallic acid	$\text{C}_6\text{H}_2 \begin{cases} \text{COOH (1)} \\ (\text{OH})_3 (3, 4, 5) \end{cases}$	220	
Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2$		
Phthalic anhydride	$\text{C}_6\text{H}_4 \begin{matrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{matrix} \text{O}$	128	

Benzamide is a crystalline substance which dissolves easily in hot water but is only slightly soluble in cold water. It is decomposed by alkali solutions, yielding ammonia.

**Benzonitrile**, (phenyl cyanide)  $\text{C}_6\text{H}_5\text{CN}$ , is obtained by heating benzamide with phosphorus pentoxide:

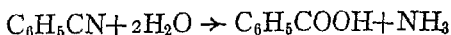


It is obtained also by fusing potassium benzene sulfonate with potassium cyanide:



It is prepared also by the Sandmeyer reaction (see Diazonium compounds, page 338).

Benzonitrile is a colorless oil which boils at  $191^{\circ}$  and has an odor resembling that of nitrobenzene. When hydrolyzed it yields benzoic acid:

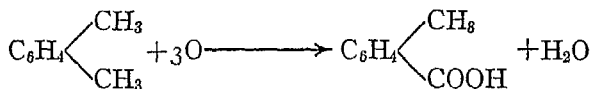


When reduced it yields benzyl amine,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ :

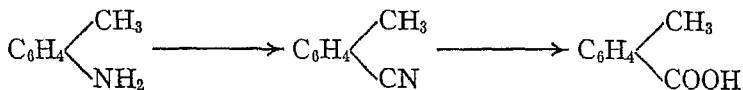


The table on pages 406-407 contains a few aromatic carboxylic acids and some of their derivatives.

**Toluic acids**,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_3 \\ \text{COOH} \end{smallmatrix}$ , are the carboxyl derivatives of toluene, having the carboxyl group united directly to the ring. They may be obtained by oxidizing the corresponding xylenes (ortho, meta, and para) with nitric acid:



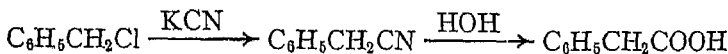
They are prepared also from the toluidines by means of the diazonium compounds (Sandmeyer's reaction):



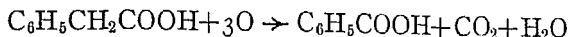
Write the complete outline equations of the series of reactions above.

These acids are crystalline compounds which have the following melting points: ortho,  $103^{\circ}$ ; meta,  $110^{\circ}$ ; para,  $180^{\circ}$ .

**Side-chain carboxylic acids.** **Phenyl acetic acid**,  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ , is the carboxyl derivative of toluene which has the carboxyl group in the side chain. It is isomeric with the three toluic acids and is obtained from benzyl chloride through the cyanide reactions:



It is a crystalline substance which melts at  $76^{\circ}$ . When oxidized with chromic acid it is converted into benzoic acid:

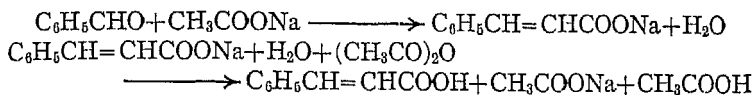


In this respect it differs from the toluic acids, which yield the phthalic acids,  $\text{C}_6\text{H}_4(\text{COOH})_2$ , when oxidized.

**Cinnamic acid**, (phenyl acrylic acid)  $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$ , is the most important of the unsaturated side-chain carboxyl acids. It occurs in storax and other balsams and in certain gums and plants. It is prepared conveniently in the laboratory by heating benzaldehyde with anhydrous sodium acetate in the presence of acetic anhydride (Perkins' synthesis).

#### EXPERIMENT 88

##### Preparation of cinnamic acid, $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$

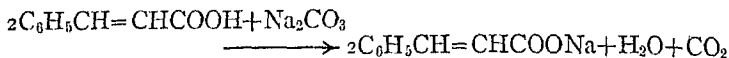


*Materials*  $\left\{ \begin{array}{l} 14 \text{ cc. benzaldehyde} \\ 7.5 \text{ grams of powdered, fused sodium acetate} \\ 21 \text{ cc. acetic anhydride} \\ \text{Sodium carbonate solution} \end{array} \right.$

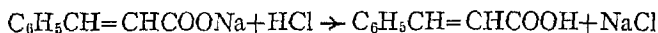
*Procedure.* Place 7.5 grams of powdered, fused sodium acetate in a 200 cc. round flask. To this add 14 cc. of benzaldehyde and 21 cc. of acetic anhydride. The flask is now immersed in an oil bath and connected to a reflux condenser. The oil bath is now heated to a temperature of  $160^{\circ}$  for about an hour, after which it is heated to  $180^{\circ}$  for about 6 hours. If the heating must be done during two laboratory periods, a calcium chloride tube containing anhydrous granulated calcium chloride should be placed in the top of the condenser to prevent access of moisture.

The apparatus is now disconnected and the hot reaction product poured into a 1.5 liter round flask. Add about 200 cc. of water. A concentrated solution of sodium carbonate is now added until the mixture is slightly alkaline. This neutralizes the excess of acetic

acid and reacts with the cinnamic acid, forming sodium cinnamate, which is more readily soluble than the cinnamic acid itself:

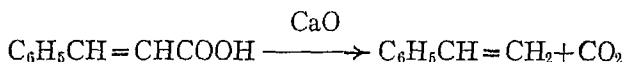


About 150 cc. of water is added and the mixture is now steam distilled to eliminate any excess of unchanged benzaldehyde. When the distillate no longer presents a milky appearance, showing that all the unchanged benzaldehyde has passed over, disconnect the apparatus. The mixture remaining in the flask is now cooled and filtered to free it from any undissolved resinous by-products. Concentrated hydrogen chloride is added to the filtrate:



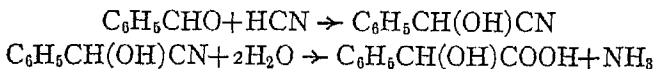
The cinnamic acid is precipitated in white, lustrous flakes. It may be purified by recrystallization from hot water. Cinnamic acid melts at 133°. Preserve a specimen and calculate the yield.

Cinnamic acid shows the behavior of an unsaturated acid. It unites with bromine, forming phenyl dibrom propionic acid,  $\text{C}_6\text{H}_5\text{CHBrCHBrCOOH}$ . When reduced with sodium amalgam and water it yields **phenyl propionic acid**, (hydrocinnamic acid)  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOH}$ , which is a crystalline substance melting at 47°. When distilled with lime, cinnamic acid yields **styrolene**, (phenyl ethylene)  $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ :



Styrolene is a colorless liquid which boils at 145°, and is an unsaturated side-chain aromatic hydrocarbon.

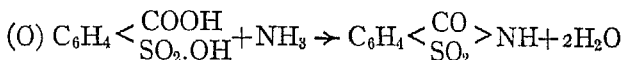
**Mandelic acid**, (phenyl glycolic acid)  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$ , contains one carbon atom united to four different groups and is an optically active carboxyl acid. It is prepared by treating hydrogen cyanide, which is obtained by the interaction of potassium cyanide and hydrogen chloride, with benzaldehyde. The nitrile thus obtained is hydrolyzed to mandelic acid:



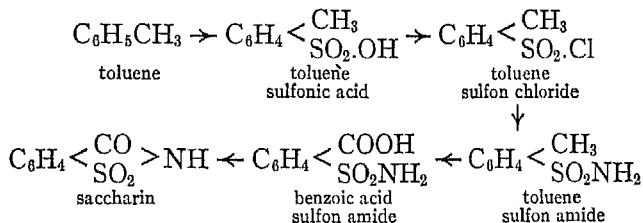
Mandelic acid is a colorless crystalline compound which melts at  $118^{\circ}$  and dissolves readily in hot water. The synthetic mandelic acid prepared in the laboratory resembles lactic acid, (methyl glycolic acid)  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , in its general behavior and is optically inactive. Synthetic inactive mandelic acid may be decomposed into the optically active dextro and levo mandelic acids by crystallizing its cinchonine salt.

### SUBSTITUTED CARBOXYL ACIDS

**Sulfo benzoic acids**,  $\text{C}_6\text{H}_4<\begin{smallmatrix} \text{COOH} \\ \text{SO}_2.\text{OH} \end{smallmatrix}$ . Ortho and para sulfo benzoic acids are obtained by oxidizing the corresponding toluene sulfonic acids,  $\text{C}_6\text{H}_4<\begin{smallmatrix} \text{CH}_3 \\ \text{SO}_2.\text{OH} \end{smallmatrix}$ . Meta sulfo benzoic acid is obtained by heating benzoic acid with sulfuric acid. Ortho sulfo benzoic, when treated with ammonia, yields **saccharin**, which is an imide (a compound containing the  $\text{NH}$  group), having the formula  $\text{C}_6\text{H}_4<\begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix}>\text{NH}$ :



Saccharin is obtained from toluene in accordance with the following outline:



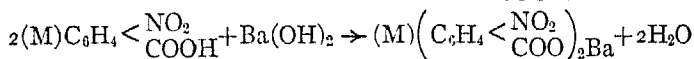
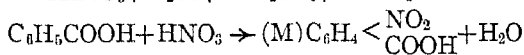
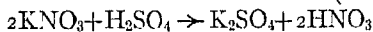
Saccharin is a crystalline substance which melts at  $224^{\circ}$ . It has a very sweet taste and is about 500 times as sweet as cane sugar. It is manufactured commercially and used for sweetening

purposes and as a substitute for sugar by persons suffering from diabetes.

**Nitro benzoic acids**,  $C_6H_4 < \begin{smallmatrix} NO_2 \\ COOH \end{smallmatrix}$ . Ortho and para nitro benzoic acids are crystalline substances which are obtained by oxidizing the corresponding nitro toluenes,  $C_6H_4 < \begin{smallmatrix} NO_2 \\ CH_3 \end{smallmatrix}$ . The ortho compound melts at  $147^\circ$  and the para compound at  $238^\circ$ . Meta nitro benzoic acid is prepared by treating benzoic acid with concentrated nitric acid, which is obtained by the interaction of potassium nitrate and sulfuric acid. When benzoic acid is nitrated in this manner, the product obtained consists mostly of meta nitro benzoic acid, although small amounts of the ortho and para compounds also are obtained.

#### EXPERIMENT 89

**Barium salt of meta nitro benzoic acid**,  $(M) \left( C_6H_4 < \begin{smallmatrix} NO_2 \\ COO \end{smallmatrix} \right)_2 Ba$



*Materials*  $\left\{ \begin{array}{l} 16 \text{ grams benzoic acid} \\ 32 \text{ grams potassium nitrate} \\ 40 \text{ cc. concentrated sulfuric acid} \end{array} \right.$

*Procedure.* Mix 16 grams of benzoic acid and 32 grams of potassium nitrate in a dry beaker. The entire mixture is now powdered in small portions in a mortar. The powdered materials are again placed in a beaker and stirred thoroughly to make a uniform mixture. 40 cc. of concentrated sulfuric acid are poured into a 300 cc. beaker and heated to a temperature of  $70^\circ$  under a hood. The dry powdered mixture of benzoic acid and potassium nitrate is now added gradually to the hot sulfuric acid, which is stirred constantly. The temperature of the sulfuric acid at this stage should not rise above  $80^\circ$ . When all of the dry mixture has been added, the temperature is raised to  $90^\circ$  and the heating continued at this temperature for about 15 min-



utes, until all the nitro benzoic acid separates as an oily layer on the surface. The mixture is now poured into a 300 cc. evaporating dish and stirred a few times, after which it is allowed to cool. When cool, the mass solidifies and the top layer of nitro benzoic acid, which has the appearance of ice, can be scraped off with a porcelain spatula or knife. Place the acid in a 500 cc. round flask, add about 300 cc. of water, and steam distil to eliminate any unchanged benzoic acid. After the acid has been steam distilled about 0.5 hour, disconnect the apparatus. The hot residue in the flask is made slightly alkaline with a filtered solution of barium hydroxide. This reacts with the nitro benzoic acid, forming the barium salt, and also acts on the potassium sulfate present, precipitating barium sulfate. Warm the flask about 0.5 hour to complete the precipitation of the barium sulfate. The hot mixture is now filtered. Should any barium sulfate pass through the filter, the filtrate should be filtered immediately. When the filtrate is cooled, the barium salt crystallizes in yellow needles. Filter, and dry on layers of filter paper.

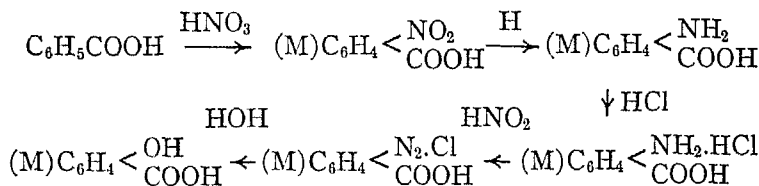
Meta nitro benzoic acid may be obtained from the barium salt by treating it with the calculated quantity of hot dilute sulfuric acid (1:10), filtering, evaporating the filtrate, and allowing the acid to crystallize. It melts at 141°. Prepare a few grams of the acid. Preserve specimens of the acid and of the barium salt.

**Amino benzoic acids,**  $C_6H_4 < \begin{smallmatrix} NH_2 \\ COOH \end{smallmatrix}$ , may be obtained by reducing the corresponding nitro benzoic acids. **Anthranilic acid** (ortho amino benzoic acid) is the most important of the amino benzoic acids. It is prepared from naphthalene,  $C_{10}H_8$ , and is a crystalline substance which melts at 144°, is soluble in water, and, like amino acetic acid, forms salts with both acids and bases. It is used in the manufacture of indigo, and certain esters of it which have a very fragrant odor are used in preparing perfumes.

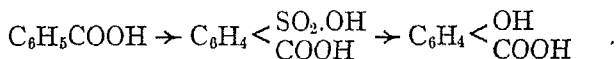
**Hydroxy acids.** There are two classes of aromatic hydroxy acids. Those containing the hydroxyl group in the side chain, such as mandelic acid,  $C_6H_5CH(OH)COOH$ , which has already been described, resemble closely the aliphatic hydroxy acids in their general behavior. Acids which contain the hydroxyl group

united directly to the ring, such as hydroxy benzoic acid,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ , are substituted acids and are called *phenolic acids*.

The phenolic acids are more important compounds than the acids containing the hydroxyl group in the side chain. **Meta hydroxy benzoic acid**,  $(\text{M})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ , may be obtained from benzoic acid through the diazonium compounds, as shown by the following outline reactions:



It is prepared also from benzoic acid by means of the sulfonic acid reactions:



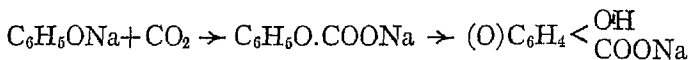
Meta hydroxy benzoic acid is a crystalline substance which melts at  $200^\circ$  and is soluble in water. It does not give a color reaction with ferric chloride.

**Para hydroxy benzoic acid**,  $(\text{P})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ , like the meta compound may be obtained from the corresponding amino benzoic acid. It is crystalline and melts at  $213^\circ$ .

**Salicylic acid**, (ortho hydroxy benzoic acid)  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$ , is the most important of the hydroxy benzoic acids. It occurs in various plants and in the oil of wintergreen (*Gaultheria procumbens*) as methyl salicylate,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{COOCH}_3 \end{smallmatrix}$ . It is obtained by oxidizing salicyl alcohol,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{CH}_2\text{OH} \end{smallmatrix}$ , or salicylic alde-

hyde,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{CHO} \end{smallmatrix}$ , with chromic acid and also by the inter-  
action of anthranilic acid,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{NH}_2 \\ \text{COOH} \end{smallmatrix}$ , and nitrous acid.

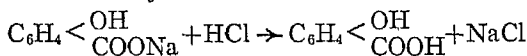
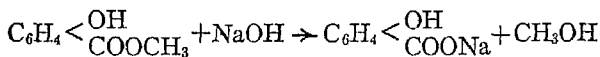
It is prepared commercially by heating sodium phenolate,  $\text{C}_6\text{H}_5\text{ONa}$ , with carbon dioxide under pressure at a temperature of about  $130^\circ$  (Kolbe's synthesis). In this method sodium phenyl carbonate,  $\text{C}_6\text{H}_5\text{O.COONa}$ , is formed as an intermediate product which is converted into sodium salicylate,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{COONa} \end{smallmatrix}$ :



It is prepared also by decomposing methyl salicylate by an alkali solution (see Experiment 29, page 137).

#### EXPERIMENT 90

**Preparation of salicylic acid,**  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{COOH} \end{smallmatrix}$



*Materials*  $\left\{ \begin{array}{l} 10 \text{ cc. of methyl salicylate} \\ 4 \text{ grams of sodium hydroxide dissolved in } 25 \text{ cc. of water} \end{array} \right.$

*Procedure.* Pour 10 cc. of methyl salicylate into a 200 cc. round flask. Add a solution of 4 grams of sodium hydroxide dissolved in 25 cc. of water. Connect the flask to a reflux condenser and boil on a wire gauze until the oil appears to be dissolved, which will require about 1.5 hours.

Disconnect the apparatus, pour the reaction product into a 300 cc. beaker, cool, and acidify with concentrated hydrogen chloride. Filter off the white precipitate of salicylic acid and recrystallize from hot water. The melting point of salicylic acid is  $156^\circ$ . Preserve a specimen.

Salicylic acid crystallizes in needles from hot water. It is soluble in hot water but only slightly soluble in cold water. It gives a violet color with ferric chloride. When neutralized with an alkali solution, salicylic acid yields metallic salts, such as sodium salicylate,  $C_6H_4 < \begin{smallmatrix} OH \\ COONa \end{smallmatrix}$ , and when treated with an excess of alkali solution, dimetallic salts like  $C_6H_4 < \begin{smallmatrix} OK \\ COOK \end{smallmatrix}$  are obtained. Esters of salicylic acid, such as methyl salicylate,  $C_6H_4 < \begin{smallmatrix} OH \\ COOCH_3 \end{smallmatrix}$ , are formed by the interaction of salicylic acid, methyl alcohol, and sulfuric acid. Salicylic acid yields also ethers,  $C_6H_4 < \begin{smallmatrix} OCH_3 \\ COOH \end{smallmatrix}$ , and ether esters,  $C_6H_4 < \begin{smallmatrix} OCH_3 \\ COOCH_3 \end{smallmatrix}$ .

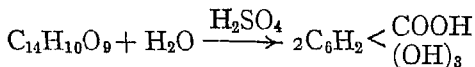
Salicylic acid is a strong antiseptic and is employed medically and in the preservation of foods. Sodium salicylate is used as an antipyretic and also as a remedy for rheumatism. Other derivatives of salicylic acid, such as phenyl salicylate, (salol)  $C_6H_4 < \begin{smallmatrix} OH \\ COOC_6H_5 \end{smallmatrix}$ , and acetyl salicylic acid, (aspirin)  $C_6H_4 < \begin{smallmatrix} OOCCH_3 \\ COOH \end{smallmatrix}$ , also are used medicinally.

**Anisic acid**, (para methoxy benzoic acid)  $(P)C_6H_4 < \begin{smallmatrix} OCH_3 \\ COOH \end{smallmatrix}$ , is obtained by oxidizing anethol,  $(P)C_6H_4 < \begin{smallmatrix} OCH_3 \\ CH=CHCH_3 \end{smallmatrix}$ , which is the principal constituent of aniseed oil. It is a crystalline substance which melts at  $185^\circ$ .

**Gallic acid**, (trihydroxy benzoic acid)  $C_6H_2 < \begin{smallmatrix} COOH (1) \\ (OH)_3 (3, 4, 5) \end{smallmatrix}$ , occurs in gallnuts and in the astringent parts of certain plants such as tea and sumach. It is prepared by boiling tannin with dilute acids. It is crystalline, melts at about  $220^\circ$  with decomposition, is soluble in water, and gives a dark-blue precipitate with ferric chloride. Gallic acid is a strong reducing agent and

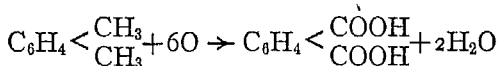
precipitates gold and silver from solutions of their salts, and reduces Fehling's solution. **Basic bismuth gallate**, (dermatol)  $C_6H_2(OH)_3COOBi(OH)_2$ , is a yellow, odorless, antiseptic powder which is used as a substitute for iodoform.

**Tannic acids**, (tannins)  $C_{14}H_{10}O_9$ , occur in gallnuts and in the barks of various trees such as hemlock and oak, from which they are extracted by boiling with water. The tannins are amorphous substances which have an astringent taste and are soluble in water. When treated with ferric chloride they yield dark-blue-colored solutions and on account of this fact are used in the manufacture of inks. When treated with gelatin or gelatin-forming tissues they form insoluble compounds. In consequence of this fact they are used in the manufacture of leather. Animal skins are prepared in a suitable manner and treated with a tannin solution. This converts the skins into a stronger material called *leather*. Tannin forms insoluble compounds with certain dyes and is therefore used as a mordant in dyeing. When tannin is boiled with dilute sulfuric acid, it is converted into gallic acid:

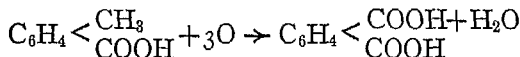


### DICARBOXYL ACIDS

**Phthalic acids**,  $C_6H_4(COOH)_2$ , are the most important of the aromatic dicarboxyl acids. They may be obtained by oxidizing the corresponding ortho, meta, and para xylenes with dilute nitric acid:

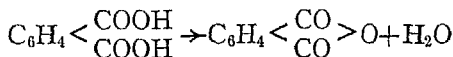


They are obtained also by oxidizing the corresponding toluic acids with alkaline permanganate solution:

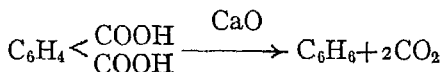
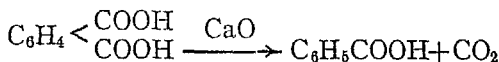


They are crystalline compounds and yield the usual derivatives of dibasic acids, such as the normal and acid salts, esters, and amides.

Ortho phthalic acid is the most important of these compounds and is usually called simply *phthalic acid*. It is prepared commercially by oxidizing naphthalene,  $C_{10}H_8$ , with concentrated sulfuric acid in the presence of mercuric sulfate. When ortho phthalic acid is heated, it is converted into phthalic anhydride,  $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>O$ :

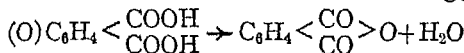


In this respect it differs from its isomers, isophthalic acid,  $C_6H_4<\begin{smallmatrix} COOH (1) \\ COOH (3) \end{smallmatrix}>$ , and terephthalic acid,  $C_6H_4<\begin{smallmatrix} COOH (1) \\ COOH (4) \end{smallmatrix}>$ , which sublime undecomposed when heated. Phthalic acid is a crystalline substance which is soluble in hot water, alcohol, and ether. Ortho phthalic acid, like its isomers, yields benzoic acid when heated carefully with lime, and when distilled with lime is converted into benzene:



#### EXPERIMENT 91

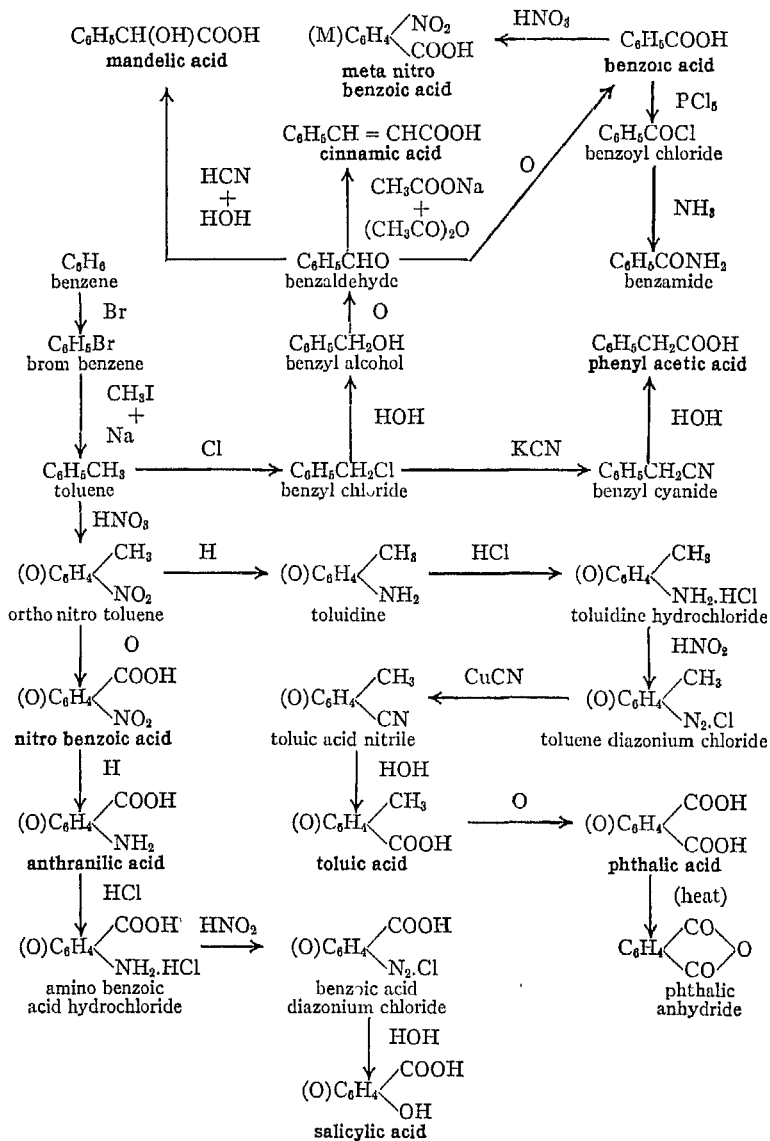
Preparation of phthalic anhydride,  $(O)C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>O$



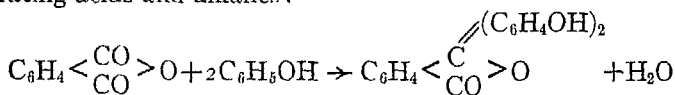
*Material.* 6 grams ortho phthalic acid

*Procedure.* Place about 6 grams of ortho phthalic acid in the middle of a dry 300 cc. evaporating dish. Place a large dry funnel over the acid. The evaporating dish is heated on a wire gauze by a small flame. The phthalic acid is converted to the anhydride, the vapors of which condense to long, flaky crystals in the upper part of the funnel. Preserve a specimen.

## AROMATIC CARBOXYL ACIDS



**Phthalic anhydride**,  $\text{C}_6\text{H}_4<\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}>\text{O}$ , obtained by heating ortho phthalic acid, is a crystalline substance which melts at  $128^\circ$ . When boiled with an alkali solution it is converted into the alkali salt of ortho phthalic acid. When phthalic anhydride is heated with phenol and concentrated sulfuric acid, it is converted into phenolphthalein, which is used as an indicator in titrating acids and alkalies:



### QUESTIONS

1. Write equations showing two general methods for preparing benzoic acid.
2. Explain, with equations, how the following compounds are prepared in the laboratory: ferric benzoate, ethyl benzoate, and benzamide.
3. Write outline equations showing the preparation of phenyl acetic acid from toluene.
4. Explain, with equations, the laboratory preparation of cinnamic acid, the barium salt of meta nitro benzoic acid, and salicylic acid.
5. Write the structural formulas of the following compounds: ortho toluic acid; benzoic anhydride; benzonitrile; mandelic acid; para sulfo benzoic acid; ortho amino benzoic acid; para hydroxy benzoic acid; salol; aspirin; gallic acid; phthalic acid.
6. For what purposes is tannic acid used?
7. How is phthalic anhydride prepared?
8. Outline the reactions indicated:
  - a. benzene  $\rightarrow$  benzyl alcohol  $\rightarrow$  mandelic acid.
  - b. toluene  $\rightarrow$  salicylic acid.

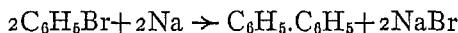


## CHAPTER TWENTY-SIX

### OTHER AROMATIC HYDROCARBONS AND DERIVATIVES

THE aromatic hydrocarbons we have studied, such as benzene and toluene, contain only one benzene ring, but there are a number of other aromatic hydrocarbons which contain two or more benzene rings. Some of these compounds are substances of considerable importance.

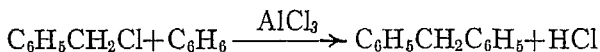
**Diphenyl**,  $C_6H_5.C_6H_5$ , is the simplest aromatic hydrocarbon containing more than one ring. It is obtained by treating an ethereal solution of brom benzene with sodium :



It is a crystalline substance which melts at  $71^\circ$ , boils at  $254^\circ$ , and when oxidized with chromic acid is converted into benzoic acid. When diphenyl is treated with halogens, nitric acid, or sulfuric acid, it yields derivatives similar to those obtained from benzene

### PHENYL DERIVATIVES OF METHANE

**Diphenyl methane**,  $\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > CH_2$ , like diphenyl, also contains two benzene rings. It may be regarded as derived from methane by substituting two phenyl groups for two atoms of hydrogen. It is prepared by treating benzene with benzyl chloride in the presence of aluminium chloride. What is the name of this synthesis?

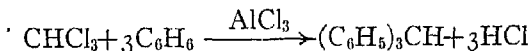


It is a crystalline substance which melts at  $26^\circ$  and when oxidized with chromic acid yields diphenyl ketone (benzophenone) :



**Triphenyl methane**,  $(C_6H_5)_3CH$ , is an aromatic hydrocarbon containing three rings. It is the parent substance of the tri-

phenyl methane dyes and on this account is an important hydrocarbon. It is obtained by treating chloroform with benzene in the presence of aluminium chloride:



It is a crystalline substance which melts at  $92^\circ$ , boils at  $358^\circ$ , and is soluble in ether and benzene. When oxidized with chromic acid it is converted into triphenyl carbinol,  $(\text{C}_6\text{H}_5)_3\text{COH}$ .

### NAPHTHALENE AND ITS DERIVATIVES

**Naphthalene**,  $\text{C}_{10}\text{H}_8$ , is the parent substance of a large number of derivatives, many of which are used in the manufacture of dyes. Naphthalene, like benzene, is therefore a substance of considerable importance. It occurs in coal tar to the extent of about 5 per cent, which is a larger proportion than that of any other hydrocarbon present in coal tar. It crystallizes from the fractional distillate of coal tar, which passes over between  $170^\circ$  and  $230^\circ$ . The crystals of crude naphthalene are pressed to free them of liquid impurities, after which they are washed with sulfuric acid. The crystals are then distilled or sublimed.

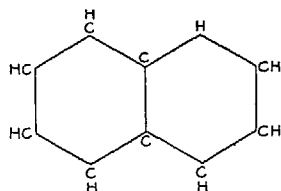
Naphthalene crystallizes in large plates which melt at  $80^\circ$  and boil at  $218^\circ$ . It is soluble in ether and hot alcohol, sublimes, is very volatile, and has a characteristic odor. It is used in the form of "moth balls" to protect woollens and furs from moths. It burns with a very luminous flame and is one of the principal illuminating constituents of coal gas. It is used principally for preparing a number of its derivatives which are employed in the manufacture of dyes.

Naphthalene resembles benzene, toluene, and other aromatic hydrocarbons in its general chemical behavior. It is a very stable substance like benzene and is not easily decomposed into simpler compounds. It interacts with nitric acid, yielding nitro derivatives, and when treated with sulfuric acid sulfonic acids

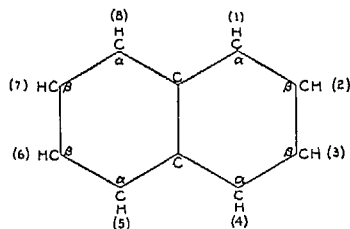
are obtained. When naphthalene is oxidized with chromic acid, it is converted into ortho phthalic acid,  $(O)C_6H_4 < \begin{smallmatrix} COOH \\ COOH \end{smallmatrix}$ :



This reaction indicates that naphthalene contains a benzene ring and another group united to the ring in the ortho position. The formula shown in Figure 38 has been found to represent in the most satisfactory manner the behavior of naphthalene. This formula represents a molecule of naphthalene as consisting of two rings united at the ortho positions. A compound having this kind of formula should yield two isomeric



Naphthalene  
Figure 38



Naphthalene  
Figure 39

monosubstitution products. This is evident from the diagram given in Figure 39, which shows that this formula contains two different sets of hydrogen atoms which are not united to the molecule in the same manner.

The hydrogen atoms, 1, 4, 5, and 8, are each connected to a carbon atom, which is in turn connected to another carbon that is common to both rings. These hydrogen atoms, therefore, have equal value and are called alpha ( $\alpha$ ) atoms.

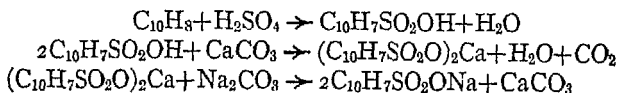
A mono derivative of naphthalene which contains a group substituted in place of one of these hydrogen atoms is called an **alpha compound**. The hydrogen atoms 2, 3, 6, and 7 are each united to the molecule in the same manner but differently from the other four hydrogen atoms. These atoms are called beta ( $\beta$ ) atoms. The formula of naphthalene therefore contains two different sets of hydrogen atoms and should yield two isomeric monosubstitution deriva-

tives. This has been found to be true experimentally. Naphthalene yields two isomeric monochlor naphthalenes, two mononitro naphthalenes, two monohydroxy naphthalenes, etc. There are other experimental facts which confirm the conclusion that naphthalene is represented in a satisfactory manner by two rings connected at the ortho positions.

**Naphthalene sulfonic acids**,  $C_{10}H_7SO_2.OH$ , are obtained by heating naphthalene with concentrated sulfuric acid. When naphthalene is sulfonated at a temperature of about  $80^\circ$ , both alpha and beta naphthalene sulfonic acids are obtained, though the chief product is the alpha compound. As the calcium salt of the alpha compound is considerably more soluble than the calcium salt of the beta compound, the alpha and beta acids may be separated by converting them into their calcium salts and crystallizing. When naphthalene is sulfonated at a temperature of about  $160^\circ$ , it is converted into beta naphthalene sulfonic acid. The alpha compound which is formed at lower temperatures is converted by an intramolecular change at the higher temperature into the beta compound. Alpha and beta naphthalene sulfonic acids are crystalline substances. The alpha compound melts at  $90^\circ$ , while the beta melts at  $161^\circ$ . The sulfonic acid derivatives of naphthalene are used considerably in the manufacture of dyes.

## EXPERIMENT 92

### Preparation of the sodium salt of beta naphthalene sulfonic acid, $C_{10}H_7SO_2ONa$



*Materials*  $\left\{ \begin{array}{l} 20 \text{ grams naphthalene} \\ 15 \text{ cc. concentrated sulfuric acid} \end{array} \right.$

*Procedure* Pour 15 cc. of concentrated sulfuric acid into a 200 cc. round flask. Place the flask upon a wire gauze and warm to a tempera-

ture of about 50°. Now add gradually, in portions of about 2 grams, 20 grams of powdered naphthalene. After the addition of each portion of naphthalene the flask should be shaken. When all the naphthalene has been added, clamp the flask to an iron stand. Place an oil bath under the flask so that the flask is partly immersed in the oil. A thermometer suspended from the iron stand is allowed to dip into the oil. The oil bath is now heated to a temperature of about 160° (not above 175°) and the heating continued at this temperature for about 3 hours. The flask is now disconnected, the oil wiped from the bottom of it, and the reaction product poured into an evaporating dish containing about 300 cc. of water. The mixture is now filtered to eliminate the excess of naphthalene, which is insoluble in water. Stir the filtrate and add powdered calcium carbonate slowly until no more carbon dioxide is evolved. The calcium carbonate reacts with the naphthalene sulfonic acid, forming the soluble calcium salt of naphthalene sulfonic acid,  $(C_{10}H_7SO_2O)_2Ca$ , and also neutralizes the excess of sulfuric acid present, precipitating calcium sulfate:

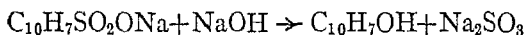


The mixture is filtered through a muslin filter, and the filtrate containing the soluble calcium salt of naphthalene sulfonic acid is now evaporated to about half its volume. The solution is now filtered through filter paper to eliminate the calcium sulfate, which, being somewhat soluble, separates as an insoluble white precipitate on concentrating the solution. A concentrated solution of sodium carbonate is now added in sufficient amount to precipitate exactly the calcium as calcium carbonate and form the sodium salt of beta naphthalene sulfonic acid. The mixture is now filtered through a muslin filter, after which it is again filtered through filter paper and the filtrate evaporated nearly to dryness in an evaporating dish which is placed on a water bath. The solution is now set aside and allowed to crystallize. Filter, and dry on layers of filter paper.

The sodium salt of beta naphthalene sulfonic acid is a crystalline substance which is soluble in water. Preserve a specimen and calculate the yield.

• Naphthols,  $C_{10}H_7OH$ , are the hydroxyl derivatives of naphthalene. Both the alpha and beta naphthols occur in coal tar and are obtained by fusing the sodium salts of the correspond-

ing alpha and beta naphthalene sulfonic acids with sodium hydroxide :



The naphthols resemble the phenols in their general chemical behavior. They give color reactions with ferric chloride, and when treated with phosphorus pentachloride yield the chlor naphthalenes,  $\text{C}_{10}\text{H}_7\text{Cl}$ . The naphthols are crystalline compounds. Alpha naphthol melts at  $95^\circ$  and boils at  $280^\circ$ . Beta naphthol melts at  $122^\circ$  and boils at  $286^\circ$ . The naphthols are used in the manufacture of dyes.

**Naphthylamines**,  $\text{C}_{10}\text{H}_7\text{NH}_2$ , are the amino derivatives of naphthalene. They may be obtained by treating the naphthols with ammonia zinc chloride (prepared by passing ammonia over anhydrous zinc chloride) :



Alpha naphthylamine is crystalline, melts at  $50^\circ$ , boils at  $300^\circ$ , and has a disagreeable odor. Beta naphthylamine is a crystalline substance which melts at  $112^\circ$ , boils at  $224^\circ$ , and is odorless. These naphthylamines are used in preparing the Congo dyes, such as Congo red.

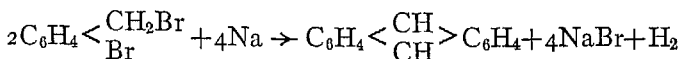
#### ANTHRACENE, ANTHRAQUINONE, AND ALIZARIN

**Anthracene**,  $\text{C}_{14}\text{H}_{10}$ , is an aromatic hydrocarbon of considerable commercial importance, as it is the substance from which the dye alizarin, or Turkey red, is prepared. It occurs in coal tar and is obtained by crystallizing the coal-tar distillate known as *anthracene oil*, which distils over above  $270^\circ$ . This anthracene distillate is purified by treating it with various solvents, after which it is steam distilled or recrystallized.

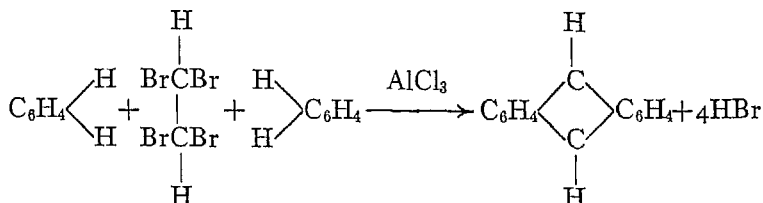
Anthracene is a crystalline substance which melts at  $213^\circ$ , boils at  $351^\circ$ , and dissolves readily in benzene.

The synthetic methods by which anthracene may be prepared

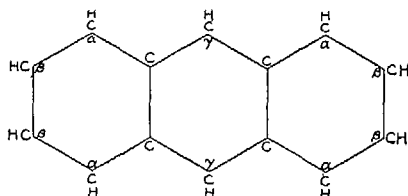
show its structure. It is obtained by treating ortho brom benzyl bromide,  $(O)C_6H_4<\begin{smallmatrix} CH_2Br \\ Br \end{smallmatrix}>$ , with sodium:



It is prepared also by treating benzene with acetylene tetrabromide in the presence of aluminium chloride:



These syntheses indicate that anthracene contains three benzene rings, as shown by the following structural formula



Anthracene  
Figure 40

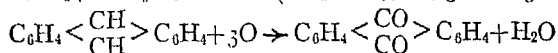
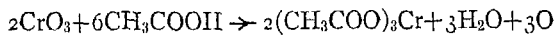
This formula of anthracene contains three different sets of hydrogen atoms, represented by the letters alpha, beta, and gamma ( $\alpha$ ,  $\beta$ , and  $\gamma$ ), and indicates that anthracene should yield three isomeric monosubstitution products.

Anthracene reacts with sulfuric acid, forming anthracene sulfonic acid, and with halogens, yielding halogen derivatives.

**Anthraquinone**,  $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_6H_4$ , is an important substance, as it is an intermediate product in the commercial preparation of the dye alizarin from anthracene. It may be prepared by various methods, one of which is the oxidation of anthracene.

## EXPERIMENT 93

Preparation of anthraquinone,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}_4$



*Materials*  $\left\{ \begin{array}{l} 5 \text{ grams anthracene} \\ 60 \text{ cc. glacial acetic acid} \\ \text{Solution containing 10 grams of chromium trioxide} \\ \text{dissolved in 10 cc. of water to which 40 cc. of glacial} \\ \text{acetic acid has been added} \end{array} \right.$

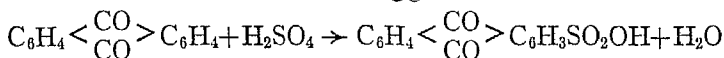
*Procedure.* Dissolve 10 grams of chromium trioxide in 10 cc. of water. Add to this solution 40 cc. of glacial acetic acid. Pour the mixture into a dry Erlenmeyer flask, place a stopper in the neck of the flask, and set aside. Now place 5 grams of anthracene in a 200 cc. round flask, and add 60 cc. of glacial acetic acid. The flask is connected to a reflux condenser and heated over a wire gauze. Boil the mixture about 20 minutes, and when most of the anthracene is dissolved, continue the boiling, and gradually pour through the top of the condenser the acetic acid solution of chromium trioxide previously prepared. The chromium solution should be introduced at short intervals in portions of about 5 cc.

When all the chromium solution has been added, continue to boil the mixture about 15 minutes to complete the oxidation of the anthracene. Disconnect the apparatus, allow the green solution to cool, and pour it into about 200 cc. of water. The anthraquinone is precipitated as a yellow or brown powder. Allow the mixture to stand about 0.5 hour to complete the precipitation of the anthraquinone. The mixture is now filtered, and washed with a small amount of hot water, then with a dilute sodium hydroxide solution (1:20), and again with water. The precipitate is dried on a porous plate or on layers of filter paper. The dry anthraquinone may be purified by sublimation in the following manner: A few grams of dried material are placed on a watch glass which is covered by filter paper. Place the watch glass on a wire gauze and heat with a very small flame. Pale-yellow needles of anthraquinone are sublimed on the filter paper.

Anthraquinone is a yellow crystalline substance which melts at  $285^\circ$  and boils at  $382^\circ$ . Calculate the yield and preserve a specimen.

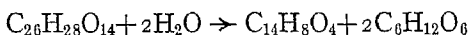


Anthraquinone is soluble in glacial acetic acid, is a very stable and odorless substance, and is not oxidized readily. It does not show the properties characteristic of quinones. It is not reduced by sulfurous acid, does not possess a pungent odor, and in other respects differs from quinones. When heated with concentrated sulfuric acid, anthraquinone yields beta anthraquinone monosulfonic acid,  $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_6H_3SO_2OH$ :

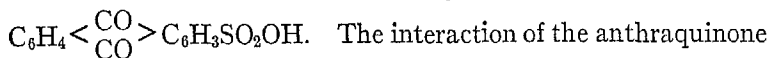


Anthraquinone yields also halogen and nitro derivatives.

**Alizarin**,  $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_6H_2<\begin{smallmatrix} OH \\ OH \end{smallmatrix}>$ , is the dihydroxy derivative of anthraquinone. It occurs in madder root as the glucoside ruberythric acid,  $C_{26}H_{28}O_{14}$ . When the glucoside is treated with ferments, dilute acids, or alkalis, it is decomposed, yielding alizarin,  $C_{14}H_8O_4$ , and glucose,  $C_6H_{12}O_6$ :

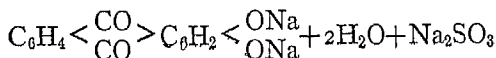
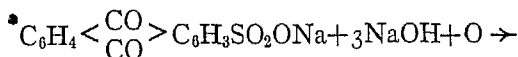
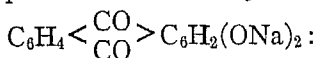


Formerly alizarin was obtained from madder, but now it is prepared commercially from anthracene. Anthracene is oxidized to anthraquinone. The anthraquinone is treated with sulfuric acid, which converts it into beta anthraquinone monosulfonic acid,

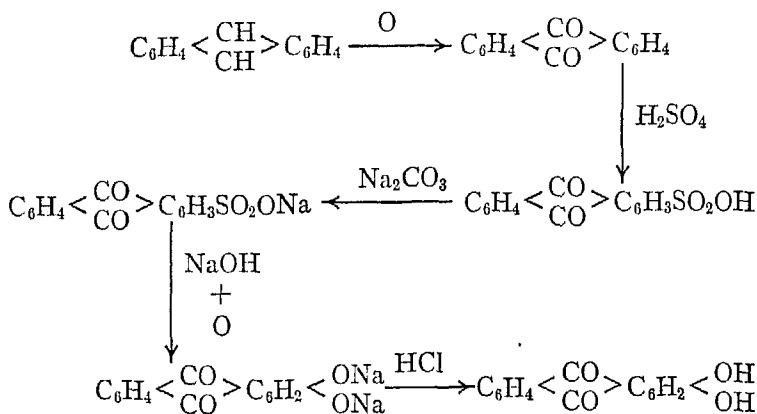


The interaction of the anthraquinone sulfonic acid and sodium carbonate yields the sodium salt of beta anthraquinone monosulfonic acid,  $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_6H_3SO_2ONa$ .

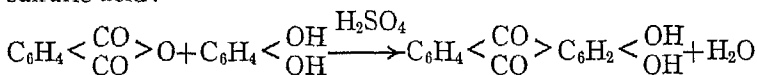
The sodium salt is then oxidized with potassium chlorate in the presence of sodium hydroxide, yielding the sodium salt of alizarin,



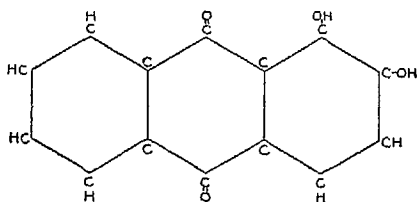
Alizarin is precipitated by treating its sodium salt with hydrogen chloride. This method of preparing alizarin from anthracene is again shown by the following outline equations:



Alizarin is prepared also by heating a mixture of phthalic anhydride,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O}$ , and catechol,  $(\text{O})\text{C}_6\text{H}_4(\text{OH})_2$ , with sulfuric acid:



This method of preparation shows that the hydroxyl groups in alizarin are in the ortho position. A further study of the nitro derivatives of alizarin shows that the structural formula of alizarin is as represented below:



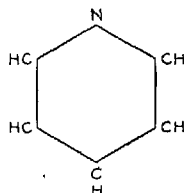
Alizarin

Figure 41

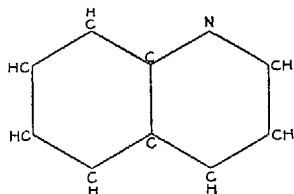
Alizarin is a red crystalline substance which melts at  $290^{\circ}$ . It is scarcely soluble in water but sublimes easily. It dissolves in alkali solutions, giving alkali salts such as the sodium salt,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}_2 < \begin{smallmatrix} \text{ONa} \\ \text{ONa} \end{smallmatrix} >$ . These alkali salts are soluble in water, yielding purple solutions which give colored precipitates with solutions of the salts of other metals, which are used as mordants. When solutions of the alkali salts of alizarin are treated with solutions of ferric salts, a violet-black precipitate is obtained; with solutions of aluminium or tin, precipitates having different shades of red are formed (Turkey red).

### PYRIDINE, QUINOLINE, AND INDIGO

**Pyridine**,  $\text{C}_5\text{H}_5\text{N}$ , is obtained from the light oil distillate of coal tar. It is obtained also from bone oil and is formed during the destructive distillation of certain organic substances. It is a liquid which boils at  $115^{\circ}$ , has an unpleasant odor, and is soluble in water. Pyridine has been prepared by various methods, which lead to the conclusion that it is represented in a satisfactory manner by the formula shown in Figure 42. Pyridine resembles the amines in that it is a strong base, gives a basic reaction with litmus, and forms salts such as pyridine hydro-



Pyridine  
Figure 42



Quinoline  
Figure 43

chloride,  $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ . It is a very stable substance and is regarded as a tertiary amine.

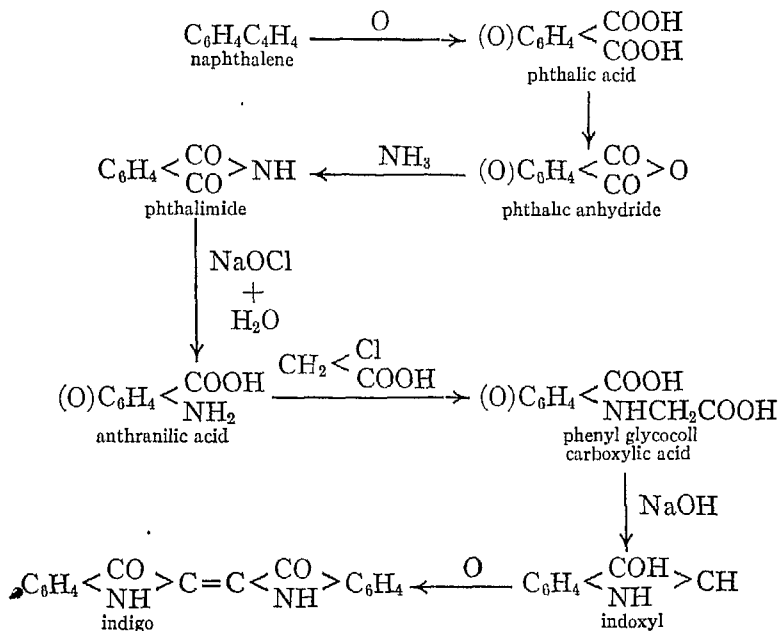
**Quinoline**,  $\text{C}_9\text{H}_7\text{N}$ , occurs in coal tar and bone oil. It is prepared by heating a mixture of aniline, glycerol, and nitro-benzene with sulfuric acid (Schraup's synthesis). It is obtained also by other syntheses, which indicate that it has the structure shown in Figure 43.

Quinoline is a colorless oil which boils at  $239^{\circ}$ , has a pleasant odor, and is somewhat soluble in water. In certain respects it shows the behavior of a tertiary base. It is a basic substance and forms salts such as the hydrochloride  $C_9H_7N.HCl$ . When quinoline is oxidized with alkaline permanganate, it is converted into quinolinic acid,  $C_8H_5N(COOH)_2$ .

**Indigo**,  $C_{16}H_{10}N_2O_2$ , is a natural dye which occurs as a glucoside in the leaves of the indigo plant. When the indigo leaves are macerated with water, the glucoside is hydrolyzed into indoxyl,  $C_8H_4<\begin{smallmatrix} C(OH) \\ NH \end{smallmatrix}>CH$ , and glucose. The indoxyl is oxidized by the atmospheric oxygen, yielding indigo, which separates as a blue precipitate. Indigo is insoluble in water and the usual organic solvents, but dissolves in aniline. It sublimes, forming a dark-blue powder. As indigo is insoluble in water, it cannot be used directly as a dye but must first be converted into a soluble derivative. A soluble form of indigo is obtained by treating it with sulfuric acid, which yields a soluble indigo sulfonic acid. This soluble form has a blue color and dyes directly. Indigo is converted also into a soluble form by reducing it with an alkaline solution of glucose which gives the leuco base, indigo white,  $C_{16}H_{12}N_2O_2$ . Indigo white is a colorless substance which dissolves, and is absorbed readily by the material to be dyed. When the material is exposed to the air, indigo white is oxidized to indigo blue, which is precipitated.

Natural indigo obtained from the indigo plant is not a pure compound but contains other coloring matters and mineral substances which affect the shade of blue. Various processes have been devised for preparing indigo synthetically. Heumann's synthesis is the most successful commercially, and synthetic indigo is now manufactured commercially and sold cheaper than natural indigo. In Heumann's synthesis of indigo, naphthalene is the material which is used in the beginning of the process. This is oxidized to ortho phthalic acid,  $(O)C_6H_4(COOH)_2$ ,

by sulfuric acid in the presence of mercuric sulfate. Phthalic acid is converted to phthalic anhydride, which when treated with ammonia yields phthalimide,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{NH}$ . Phthalimide is converted to anthranilic acid,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{COOH} \\ \text{NH}_2 \end{smallmatrix}$ , by treating with an alkali hypochlorite solution. Anthranilic acid reacts with chloroacetic acid, giving the orthocarboxyl acid of phenyl glycocoll,  $(\text{O})\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{COOH} \\ \text{NHCH}_2\text{COOH} \end{smallmatrix}$ . This substance, fused with alkalis, gives indoxyl,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{COH} \\ \text{NH} \end{smallmatrix} > \text{CH}$ , which in alkaline solution is oxidized to indigo by atmospheric oxygen. These various transformations are indicated by the following outline:



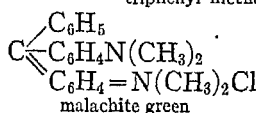
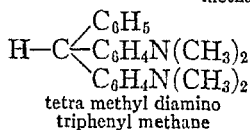
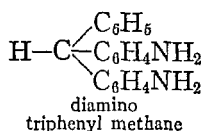
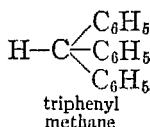
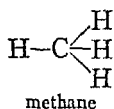
The solution of the indigo problem was accomplished by the work of many chemists, who worked on this problem about 20 years.

The process outlined above is called Heumann's synthesis because Heumann discovered that indigo could be obtained from phenyl glycocoll carboxylic acid.

### DYES

Dyes are compounds which are used to color various materials such as cotton, linen, wool, and silk. A number of plants yield colored solutions which are capable of dyeing materials under the proper conditions. Several of these natural dyes, such as indigo and alizarin, which are obtained from plants have been used for many years. Synthetic dyes are those which are manufactured commercially. Some of the natural dyes, such as indigo and alizarin, are also prepared synthetically for commercial use. Synthetic dyes have certain advantages over the natural dyes. They are usually of better quality because we can control laboratory conditions, such as the weights of reacting substances, temperature, time, methods of purification, and analysis, and consequently produce a dye of uniform composition. There are a large number of dyes, and these are divided into different groups.

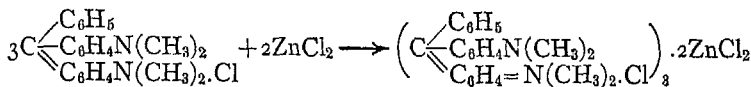
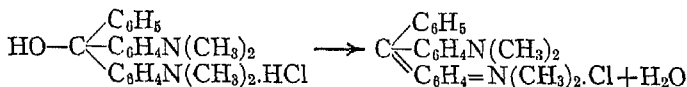
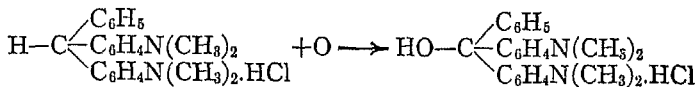
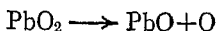
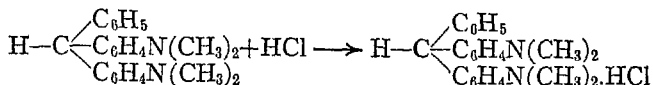
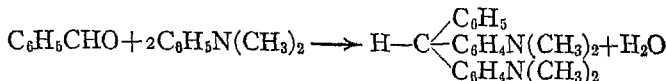
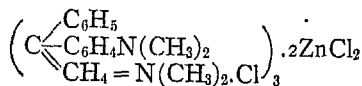
**Triphenyl methane dyes.** Triphenyl methane,  $(C_6H_5)_3CH$ , is the parent substance of a number of compounds known as the triphenyl methane dyes. **Malachite green** is one of the most important members of this group. The relations between methane, triphenyl methane, and malachite green are shown by the following formulas :



Commercial malachite green (zinc double salt of malachite green) is prepared from benzaldehyde and dimethyl aniline.

## EXPERIMENT 94

## Zinc double salt of malachite green

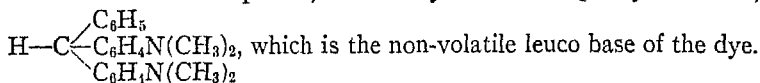


*Materials* {
 

- 20 grams zinc chloride
- 21 cc. dimethyl aniline
- 10 cc. benzaldehyde
- Solution of 5 cc. concentrated hydrogen chloride dissolved in 10 cc. water
- Solution of 2 cc. glacial acetic dissolved in 3 cc. water
- 4 grams lead peroxide
- 10 grams sodium sulfate
- 8 grams zinc chloride

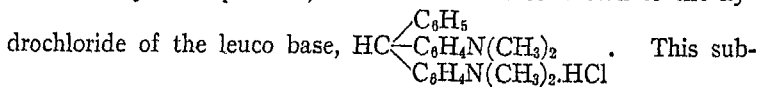
*Procedure.* Heat 20 grams of zinc chloride, with constant stirring, in a porcelain dish over a wire gauze until the mass is fused. The dish is now cooled and the mass scraped into a porcelain mortar and powdered, after which it is placed in a 500 cc. evaporating dish. To this are added 21 cc. of dimethyl aniline and 10 cc. of benzaldehyde. The dish containing these materials is placed upon an actively boiling water bath and stirred constantly for about 2 hours, until the odor

of benzaldehyde has disappeared and a deep-green viscous mass is obtained. About 300 cc. of boiling water is now added. Continue to heat on the water bath, with constant stirring, for about 10 minutes, and when the mass is melted pour it into a liter flask. Add about 100 cc. of water. The mixture is now steam distilled until no more oily drops of dimethyl aniline pass over. The viscous mass remaining in the flask is the compound, tetramethyl diamino triphenyl methane,



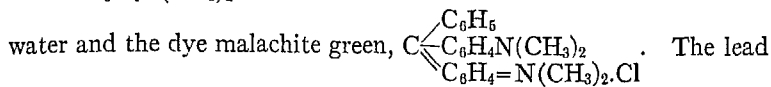
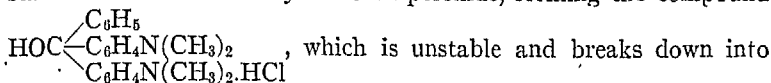
Disconnect the apparatus, and allow the flask to cool. The supernatant aqueous liquid is now poured off and the leuco base washed several times with water by decantation. The flask is placed again on a boiling water bath and a sufficient amount of alcohol (95 per cent) added to dissolve the base. The solution is now filtered into a 500 cc. flask, which is corked and allowed to stand over night. The leuco base separates in colorless crystals, which are filtered off, washed with a very small amount of alcohol, and dried in the air on several layers of filter paper. By concentrating the filtrate a second yield of crystals may be obtained. The yield of leuco base is nearly theoretical. Sometimes the leuco base does not crystallize but separates as an oil. This is due to the fact that the alcoholic solution is too concentrated. In this case more alcohol is added, the solution warmed until the mixture is dissolved, and the solution again allowed to crystallize.

The leuco base is oxidized and converted into the zinc double salt of malachite green in the following manner: 10 grams of the dry base are placed in a 200 cc. beaker. To this is added a solution of hydrogen chloride prepared by adding 5 cc. of concentrated hydrogen chloride to 10 cc. of water. The mixture is warmed until the base is dissolved. This colorless solution of the base is then diluted in a 2 liter flask with 800 cc. of water and treated with a solution containing 2 cc. of glacial acetic acid dissolved in 3 cc. of water. The mixture is cooled with a few lumps of ice. Add gradually, with frequent shaking, a paste of lead peroxide prepared by treating 4 grams of lead peroxide,  $\text{PbO}_2$ , with a sufficient amount of water to form a thin paste. The mixture is allowed to stand about 5 minutes, with occasional shaking. As shown by the equations, the leuco base is converted to the hy-

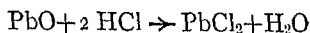




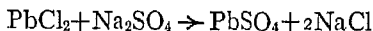
stance is then oxidized by the lead peroxide, forming the compound



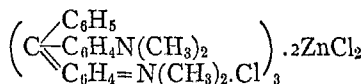
oxide present, which is obtained by the reduction of the lead peroxide, unites with hydrogen chloride, precipitating lead chloride:



As lead chloride is somewhat soluble in water, a solution containing 10 grams of sodium sulfate dissolved in 50 cc of water is now added to precipitate the soluble lead salts, and the precipitated lead sulfate and lead chloride are filtered off:



To the filtrate is added a solution of zinc chloride prepared by treating 8 grams of zinc chloride with a sufficient amount of water to dissolve it. The zinc chloride unites with the dye, forming the zinc double salt of malachite green:



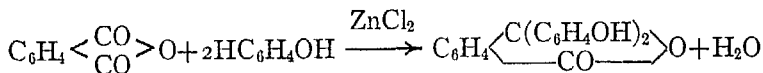
A saturated solution of sodium chloride is now added until all the dye is precipitated, after which it is filtered, washed with a small quantity of saturated sodium chloride solution, and dried on a porous plate or on several layers of filter paper. Preserve a specimen.

A. Prepare a dye bath of malachite green by dissolving about 0.5 gram of the zinc double salt of malachite green in about 50 cc. of water. Dye strips of silk by immersing them in this dye bath.

There are a number of dyes closely related to malachite green. These are obtained by treating dimethyl aniline, or other substituted anilines, with benzaldehyde or substituted benzaldehydes. Brilliant green is obtained by treating benzaldehyde with diethyl aniline.

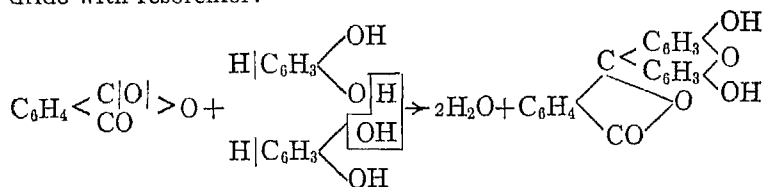
The phthaleins constitute a group of dyes which also are regarded as derivatives of triphenyl methane.

**Phenolphthalein**,  $C_6H_4 \langle \text{C}(\text{C}_6\text{H}_4\text{OH})_2 \rangle \text{O}$ , is obtained by heating phthalic anhydride with phenol in the presence of zinc chloride:

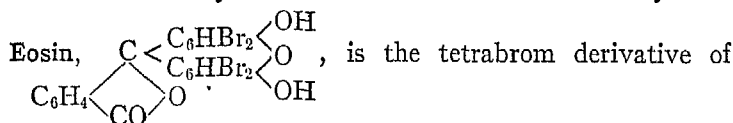


Phenolphthalein is a crystalline substance which melts at  $250^\circ$ . It dissolves readily in hot alcohol but is only slightly soluble in water. Acid and neutral solutions of phenolphthalein are colorless, but alkaline solutions are red; hence phenolphthalein is used as an indicator in titrating acids and alkalis. It has no value as a dye.

**Fluorescein**,  $\text{C}_{20}\text{H}_{12}\text{O}_5$ , is prepared by heating phthalic anhydride with resorcinol:

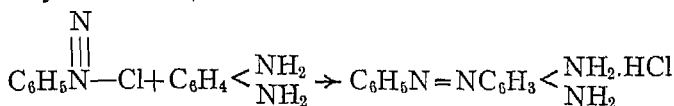


Fluorescein is soluble in alcohol but only slightly soluble in water. It dissolves readily in alkalis. When the alkali solutions are diluted, they show a beautiful yellowish-green fluorescence. Fluorescein yields derivatives which are used as dyes.



fluorescein. It is prepared by treating fluorescein with bromine. It is a red crystalline substance soluble in alcohol but difficultly soluble in water. It dissolves in alkali solutions which when diluted show a green fluorescence. Eosin yields derivatives which are dyes.

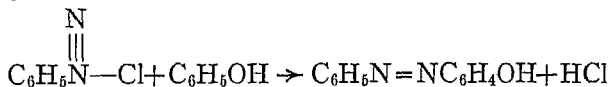
**Azo dyes** form one of the most important groups of synthetic dyes. They may be regarded as derivatives of azo benzene,  $C_6H_5N=NC_6H_5$ , which is the simplest of the azo compounds. Azo dyes are prepared by treating diazonium salts with aromatic amines or phenols. Thus, when phenyl diazonium chloride,  $C_6H_5N_2Cl$ , is treated with meta phenylenediamine,  $(M)C_6H_4(NH_2)_2$ , diamino azo benzene hydrochloride (chrysoidine hydrochloride) is obtained:



Chrysoidine hydrochloride is a crystalline substance soluble in water. It is a yellow dye and dyes wool and silk directly and cotton goods after they have been mordanted with tannin.

Helianthin, (dimethyl amino azo benzene sulfonic acid)  $HO.O_2S.C_6H_4N=NC_6H_4N(CH_3)_2$ , is an amino azo dye. It is prepared by diazotizing sulfanilic acid and treating the reaction product with dimethyl aniline hydrochloride. The sodium salt of helianthin is known as methyl orange. Methyl orange is a yellow powder which dissolves readily in hot water, giving a yellow solution. This aqueous solution is colored red by acids, and consequently methyl orange is used as an indicator in volumetric analysis.

**Hydroxy azo benzene**,  $C_6H_5N=NC_6H_4OH$ , is obtained by treating phenyl diazonium chloride with phenol:



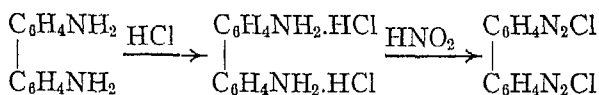
By what series of reactions could you prepare the following compounds from benzene? azo benzene; phenyl diazonium chloride; meta phenylene diamine.

Hydroxy azo benzene yields a number of important derivatives which are used as dyes. The preparation of hydroxy azo dyes consists in treating a cool alkaline solution of phenol, or

phenol sulfonic acid, with a diazonium chloride solution which has been cooled with ice. When the solutions have been mixed, the dye is precipitated (salted out) by adding a concentration solution of sodium chloride.

Most aromatic amines may be diazotized, yielding diazonium salts, which when treated with aromatic amines, or phenols, form azo compounds. Thus a large number of azo compounds may be prepared. Many of these are important dyes.

**Congo dyes.** Benzidine,  $\begin{array}{c} \text{C}_6\text{H}_4\text{NH}_2 \\ | \\ \text{C}_6\text{H}_4\text{NH}_2 \end{array}$ , when diazotized yields diphenyl tetrazonium chloride,  $\begin{array}{c} \text{C}_6\text{H}_4\text{N}_2\text{Cl} \\ | \\ \text{C}_6\text{H}_4\text{N}_2\text{Cl} \end{array}$ . This substance contains two diazo groups and is known as a tetrazo compound:



This tetrazo compound, like other diazonium salts, reacts with aromatic amines, or phenols, and their sulfonic acid derivatives, producing a variety of compounds known as Congo dyes.

**Congo red**,  $\begin{array}{c} \text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_6\text{NH}_2\text{SO}_2\text{ONa} \\ | \\ \text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_5\text{NH}_2\text{SO}_2\text{ONa} \end{array}$ , is prepared by treating diphenyl tetrazonium chloride with naphthylamine sulfonic acid,  $\text{C}_{10}\text{H}_6\text{NH}_2\text{SO}_2\text{OH}$  (1 : 4). It is a scarlet powder. Acid solutions of Congo red are blue, while alkaline solutions are red. Congo red is a good indicator for certain titrations in volumetric analysis. Alkaline solutions of Congo red dye cotton goods a red shade, without the aid of a mordant.

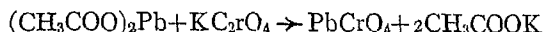
## DYEING

Dyeing consists in depositing an insoluble substance upon the fiber of a material so that the color is "fast," or permanent,

and is not removed by washing. Materials are dyed because dyed materials are not so easily soiled and have pleasing colors. Dyes are colored compounds which either are soluble in water or may be converted into a soluble form. The process of dyeing with mineral dyes presents, perhaps, the simplest example of dyeing. This consists simply in immersing the fabric in the bath of some metallic salt, after which it is placed in a second bath containing a solution which precipitates the salt in the first solution. Thus an insoluble precipitate is deposited upon the fiber of the material.

#### EXPERIMENT 95

**Dyeing by precipitation with chrome yellow,  $\text{PbCrO}_4$**



*Materials* { Lead acetate solution (4 grams in 100 cc.)  
Potassium chromate solution (4 grams in 80 cc.)

*Procedure.* A few strips of cheesecloth are boiled in a dilute soap solution to free the cotton fiber from any adhering grease. The strips are now removed and washed thoroughly with water. Prepare a bath of lead acetate by treating 4 grams of lead acetate with 100 cc. of water and filtering the solution.

A bath of potassium chromate is now prepared by dissolving 4 grams of potassium chromate in 80 cc. of water. Heat these two baths to a temperature of about  $80^\circ$ . Immerse a strip of cheesecloth in the lead acetate bath and then in the chromate bath. Chrome yellow,  $\text{PbCrO}_4$ , is precipitated on the fiber of the material. The dyed material should be hung up and allowed to dry.

**Substantive dyes, adjective dyes, and mordants.** There are two classes of synthetic dyes, which are called substantive and adjective. Adjective dyes do not combine directly with fibers, but require the aid of a mordant to make them adhere to the fiber. **Mordants**, then, are substances which form insoluble compounds with the adjective dyes. Substantive dyes adhere directly to the fiber of the material to be dyed. Congo red, for

example, is a substantive dye for cotton and woolen goods. Salts are often added to the dye bath to render the precipitated dyes more insoluble and to produce a more permanent color.

#### EXPERIMENT 96

##### Dyeing with a substantive dye

(Congo red)

*Materials* { Congo red bath (0.5 gram in 100 cc.)  
Sodium carbonate solution (0.5 gram in 50 cc.)  
Sodium sulfate solution (0.5 gram in 50 cc.)

*Procedure.* Prepare a bath of Congo red in the following manner: Dissolve about 0.5 gram of the dye in 100 cc. of water. Add to this a solution of 0.5 gram of sodium carbonate dissolved in about 50 cc. of water. To this mixture is added a solution of 0.5 gram of sodium sulfate dissolved in 50 cc. of water. Heat this bath to a temperature of about 80° and immerse in it a strip of cheesecloth. Allow the cloth to remain in the bath a few minutes; then remove it and wash with water. The dye combines with the fiber of the material, forming an insoluble, red-colored precipitate, thus producing a "fast" color which is not removed by washing.

In dyeing with adjective dyes, various substances, such as tannic acid and the acetates, or other salts, of iron, aluminium, and chromium, are used as mordants. Acid mordants such as tannic acid are used with basic dyes like malachite green. The material to be dyed is treated first with a tannic acid solution, after which it is immersed in a solution of tartar emetic which converts the tannic acid into an insoluble antimony salt of tannic acid. This treatment precipitates the mordant upon the fiber. The mordanted material is now dyed by immersing it in the dye bath, which precipitates the insoluble colored compound.

Basic mordants, such as the acetates of iron and aluminium, are used with acid dyes like picric acid.

## EXPERIMENT 97

## Dyeing with an adjective dye

(Malachite green)

*Materials* { Solution of tannic acid (0.5 gram in 100 cc.)  
 { Solution of tartar emetic (0.3 gram in 200 cc.)  
 { Solution of malachite green (0.1 gram in 400 cc.)

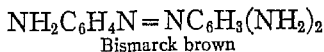
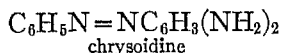
*Procedure.* Prepare a tannic acid bath by dissolving 0.5 gram of tannic acid in about 100 cc. of water. A bath of tartar emetic is prepared by dissolving 0.3 gram of tartar emetic in 200 cc. of water. A dye bath of malachite green is now made by dissolving 0.1 gram of malachite green in about 400 cc. of water.

Place a strip of cheesecloth in the tannic acid bath, and allow it to remain there about 5 minutes. The strip is now removed and placed in the tartar emetic bath and allowed to remain there about 10 minutes to precipitate the mordant, which is an antimony salt of tannic acid. The strip which has been mordanted is now placed in the cold malachite green bath, which is now heated gradually to a temperature of 60°. The dyed strip is now removed and washed with running water.

Some dyes are substantive for certain materials, and adjective for others. Malachite green is substantive for silk and woollen goods and adjective for cotton materials.

A dye usually forms different colors when used with different mordants. Calico mordanted with an aluminium salt is dyed red with alizarin, but when mordanted with an iron salt it is dyed purple by alizarin. Thus many different shades of colors may be obtained by varying the dyes and mordants.

The color of a dye is often modified by introducing into it other groups such as phenyl, methyl, amino, etc. With increase in molecular weight the shade of the dye usually becomes darker. Thus chrysoidine (diamino azo benzene) is yellow, while Bismarck brown (triamino azo benzene) is a brown dye:



Dyes usually contain certain chromophore or color groups, such as nitro ( $\text{NO}_2$ ) and azo ( $\text{N}=\text{N}$ ). They contain also auxochrome groups, such as phenol ( $\text{OH}$ ) or amino ( $\text{NH}_2$ ), which are acid or basic. These auxochrome groups give the dye the property of combining with the fiber or mordant.

**Leuco compounds.** Dyes are often converted into colorless compounds when reduced. Frequently these reduced colorless compounds are again converted readily into the original dyes when oxidized. These colorless reduction products which behave in this manner are called *leuco compounds*. When the dye is insoluble and its leuco compound is soluble, the dye is applied to the fabric in the form of its soluble leuco compound, after which the leuco compound is allowed to oxidize to the insoluble dye. Indigo is an example of this class of dyes. When indigo is reduced it is converted into the soluble leuco compound, indigo white. The fabric to be dyed is immersed in a solution of indigo white, after which it is exposed to the air and the indigo white is oxidized to insoluble indigo blue.

### TERPENES

When certain plants such as the conifer and citrus species are steam distilled, they yield volatile, or essential, oils which contain hydrocarbons known as the *terpenes*. The terpenes form a large group of compounds, some of which are of considerable importance.

**Turpentine** is one of the most abundant of the essential oils. When certain pine trees, or conifers, are cut, a liquid flows out which is called *oil of turpentine*. Turpentine is a solution of resin dissolved in a volatile oil. When it is steam distilled, the volatile oil passes over, leaving the resin. Turpentine is a colorless oil which boils at about  $160^\circ$  and dissolves in most organic solvents, but is insoluble in water. It is used as a solvent for oils and resins and in the preparation of varnishes and paints.

**Pinene**,  $\text{C}_{10}\text{H}_{16}$ , is one of the most important of the terpene



hydrocarbons and is the principal constituent of oil of turpentine. When turpentine is distilled, pinene passes over at  $155^{\circ}$ . Pinene is a colorless liquid, has the odor of turpentine, and distills with steam. Pinene obtained from American turpentine has a dextro rotation, while the French turpentine yields a levo pinene. Pinene is an unsaturated hydrocarbon and unites with bromine, forming a dibromide,  $C_{10}H_{16}Br_2$ , and with hydrogen chloride, yielding pinene hydrochloride,  $C_{10}H_{17}Cl$ . Pinene hydrochloride is a white crystalline substance which melts at  $131^{\circ}$  and has an odor somewhat like that of camphor. It is called *artificial camphor*.

**Camphene**,  $C_{10}H_{16}$ , is a terpene hydrocarbon which is obtained from certain essential oils and by treating pinene hydrochloride with alkalis. It is a solid substance which melts at  $48^{\circ}$  and boils at  $160^{\circ}$  and, like pinene, forms a dibromide and a hydrochloride. When oxidized it yields camphor.

**Camphors** are crystalline substances containing oxygen. They are related to the terpenes. Camphor,  $C_{10}H_{16}O$ , is the ordinary or common variety. It is obtained by steam distilling the wood and leaves of the camphor tree which grows in Japan and Formosa. The crude camphor is purified by sublimation. Ordinary camphor melts at  $176^{\circ}$ , has a dextro rotation, and has a characteristic odor. It is soluble in alcohol and other organic solvents, but is only slightly soluble in water. It is used medicinally and also in the preparation of celluloid.

Camphor may be prepared synthetically from turpentine in the following manner: The turpentine is distilled, yielding pinene. Pinene reacts with hydrogen chloride, giving pinene hydrochloride, which when treated with alkalis yields camphene. Camphene is converted into camphor when oxidized.

**Borneo camphor**,  $C_{10}H_{18}O$ , occurs in a camphor tree (*Dryobalanops camphora*) which is found in Borneo and Sumatra. It is a crystalline substance which melts at  $203^{\circ}$ , has a dextro rotation, and has an odor somewhat like that of ordinary camphor.

## OTHER AROMATIC HYDROCARBONS AND DERIVATIVES

NAME	FORMULA	MELTING POINT, °C.	BOILING POINT, °C.
Diphenyl	$C_6H_5.C_6H_5$	71	254
Diphenyl methane	$C_6H_5CH_2C_6H_5$	26	
Triphenyl methane	$(C_6H_5)_3CH$	92	358
Naphthalene	$C_{10}H_8$	80	218
Naphthalene sulfonic acid	$C_{10}H_7SO_2OH$		
Naphthol	$C_{10}H_7OH$		
Naphthylamine	$C_{10}H_7NH_2$		
Anthracene	$C_6H_4 < \begin{smallmatrix} CH \\ CH \end{smallmatrix} > C_6H_4$	213	351
Anthraquinone	$C_6H_4 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_4$	285	382
Alizarin	$C_6H_4 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_2 < \begin{smallmatrix} OH \\ OH \end{smallmatrix}$	290	
Pyridine	$C_5H_5N$		115
Quinoline	$C_9H_7N$		239
Indigo	$C_6H_4 < \begin{smallmatrix} CO \\ NH \end{smallmatrix} > C=C < \begin{smallmatrix} CO \\ NH \end{smallmatrix} > C_6H_4$		
Malachite green	$C_6H_5C < \begin{smallmatrix} C_6H_4N(CH_3)_2 \\ C_6H_4=N(CH_3)_2.Cl \end{smallmatrix}$		
Phenolphthalein	$C_6H_4 < \begin{smallmatrix} C(C_6H_4OH)_2 \\ CO \end{smallmatrix} > O$	250	
Chrysoidine hydrochloride	$C_6H_5N=NC_6H_3 < \begin{smallmatrix} NH_2.HCl \\ NH_2 \end{smallmatrix}$		
Pinene	$C_{10}H_{16}$		155
Camphene	$C_{10}H_{16}$	48	160
Camphor	$C_{10}H_{16}O$	176	

## GLUCOSIDES, ALKALOIDS, AND PROTEINS

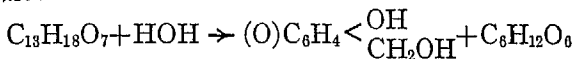
**Glucosides** are complex substances which occur in plants. They are decomposed by enzymes or dilute acids, yielding chiefly glucose and various other products. We have already had occasion to refer to some of these substances (pages 78 and 273).

**Amygdalin**,  $C_{20}H_{27}NO_{11}$ , occurs in bitter almonds and in the kernels of cherries, peaches, and other fruits. When the substances which contain amygdalin are boiled with dilute acid, the amygdalin is decomposed, yielding benzaldehyde, glucose, and hydrogen cyanide:



When amygdalin is allowed to stand in contact with water, it also is decomposed in accordance with the equation above by the enzyme emulsin which occurs in bitter almonds.

**Salicin**,  $C_{13}H_{18}O_7$ , occurs in the bark and leaves of the willow. It is decomposed by dilute acids or enzymes into glucose and salicyl alcohol:



**Alkaloids** are certain nitrogenous substances which occur in plants. Many of them, when taken internally, have a decided physiological action, and they are sometimes called the "active principles of plants." On account of their remarkable physiological properties many of them are used extensively in medicine, and they are therefore substances of unusual interest. Most of the alkaloids are crystalline substances, though a few are liquids. Many of them are poisonous, have a bitter taste, and are optically active, having a levo rotation. They are usually soluble in alcohol, ether, and other organic solvents, but are only slightly soluble in water. They are basic substances and when treated with acids yield crystalline salts. Most alkaloids are precipitated by certain reagents, such as tannic, picric, and molybdic acids,

and double salts like mercuric potassium iodide. These reagents are often used to separate the alkaloids from their solutions. Many alkaloids give characteristic color reactions with chlorine, water and nitric and sulfuric acids, and these reagents may therefore be used in their identification.

**Coniine**,  $C_8H_{17}N$ , occurs in certain species of hemlock. It is a colorless oil which boils at  $167^\circ$ . It is a very poisonous substance having a strong odor, is a strong base, and forms the hydrochloride  $C_8H_{17}NHCl$ .

**Nicotine**,  $C_{10}H_{14}N_2$ , occurs in tobacco leaves. It is a colorless oil which boils at  $247^\circ$ . It is a basic substance soluble in water.

**Atropine**,  $C_{17}H_{23}NO_3$ , occurs in belladonna, or deadly nightshade. It is a crystalline substance, melts at  $115^\circ$ , and is soluble in alcohol and ether. It is a basic substance, forming salts, is very poisonous, and when dropped into the eye has the property of dilating the pupil. It is used considerably by oculists.

**Cocaine**,  $C_{17}H_{21}NO_4$ , occurs in coca leaves. It is crystalline, melts at  $98^\circ$ , forms salts, and is used as a local anesthetic.

**Quinine**,  $C_{20}H_{24}N_2O_2$ , occurs with other alkaloids in Peruvian bark. It is a basic crystalline substance which melts at  $177^\circ$ . It is used medicinally as quinine sulfate in cases of malarial fever and for other purposes.

**Cinchonine**,  $C_{19}H_{22}N_2O$ , occurs in cinchona bark. It is crystalline and melts at  $255^\circ$ . It has antipyretic properties and is used also to separate optically inactive compounds into their optically active varieties.

**Strychnine**,  $C_{21}H_{22}N_2O_2$ , is present in the seeds of *Strychnos nux-vomica*. It is a crystalline substance and melts at  $284^\circ$ . It is a strong nervous stimulant and is used medicinally in the form of strychnine sulfate.

**Morphine**,  $C_{17}H_{19}NO_3$ , is the principal alkaloid of opium. It is a crystalline substance and is used medicinally as a soporific.

. **Proteins** are certain complex organic compounds which occur in plants and animals. The simple proteins contain carbon, hydrogen, oxygen, nitrogen, and sulfur. They are colloidal substances having large molecular weights and are usually classified according to their physical properties, such as their differences in solubility. When proteins are hydrolyzed, amino acids such as amino acetic acid,  $\text{CH}_2 < \begin{smallmatrix} \text{NH}_2 \\ \text{COOH} \end{smallmatrix}$ , are obtained.

Polypeptides and other complex substances are formed as intermediate products in this hydrolyzing process. As examples of proteins may be mentioned egg albumen or the white of an egg. Egg albumen belongs to a class of proteins called *albumens*, which are soluble in water and coagulated by heat. The pigment of red blood corpuscles is the protein hæmoglobin, which belongs to the group known as *hæmoglobins*. Hæmoglobin unites with oxygen, yielding compounds which are decomposed easily. It is the oxygen carrier of the body.

**Revised nomenclature.** In order to save space, symbols instead of formulas or names are frequently used in chemical journals. Thus the names of the following radicals have been abbreviated as shown below :

$\text{CH}_3$	methyl	Me
$\text{C}_2\text{H}_5$	ethyl	Et
$\text{CH}_3\text{CH}_2\text{CH}_2$	propyl (normal)	$\text{Pr}^\alpha$
$(\text{CH}_3)_2\text{CH}$	propyl (iso)	$\text{Pr}^\beta$
$\text{CH}_3\text{CO}$	acetyl	Ac
$\text{C}_6\text{H}_5$	phenyl	Ph
$\text{C}_6\text{H}_5\text{CO}$	benzoyl	Bz

According to this abbreviated system of nomenclature the formula of ether is  $\text{Et}_2\text{O}$ , of methyl alcohol  $\text{MeOH}$ , and of acetic acid  $\text{ACOH}$ .

## QUESTIONS

1. Write the structural formulas of the following compounds: diphenyl; diphenyl methane; triphenyl methane; naphthalene; anthracene.
2. Explain briefly how the following compounds are prepared: sodium salt of beta naphthalene sulfonic acid; anthraquinone.
3. For what purposes are alizarin, indigo, and malachite green used?
4. Write the structural formulas of alpha naphthol; beta naphthylamine; pyridine; quinoline.
5. What is meant by dyeing, substantive dyes, adjective dyes, and mordants?
6. Mention some of the important groups of dyes and give examples of each group.
7. What are azo dyes, and how are they prepared?
8. What kind of compounds are the following: terpenes, glucosides; alkaloids; proteins? Give examples of each of these classes of compounds.

## APPENDIX

### I. GENERAL LABORATORY DIRECTIONS

At the beginning of the course a desk will be assigned to each student, and in this desk will be found most of the apparatus necessary for the experiments and also a printed list of this equipment. Each student should check this list and note any articles that may be missing. If a student is unacquainted with the names of various articles, the necessary information may be obtained from one of the instructors. It is important to check the apparatus accurately, as each student is responsible for the equipment that is assigned to him. The corrected list should be given to the stock-room clerk.

**Cleaning apparatus.** Prepare a cleaning solution in the following manner: Place 25 grams of potassium dichromate in an evaporating dish, and add to it 50 cc. of water. To this mixture add slowly 30 cc. of concentrated sulfuric acid. Stir until the chromate has dissolved. Porcelain and glass apparatus should be cleaned with this solution, after which the cleaning solution should be poured into a bottle, which is then stoppered and set aside for future use. Apparatus which has been cleaned in this solution should then be washed thoroughly with running water. Articles such as beakers, flasks, evaporating dishes, and test tubes should be placed in the desk in an inverted position, so that they will dry easily. In preparing organic compounds it frequently happens that good results are obtained only in the absence of water. Again, many organic solvents, or compounds, are not soluble in water, and it is thus often very essential to have all vessels dry before beginning an experiment. A rapid method of drying vessels such as flasks is to wash with water; then rinse with a small amount of alcohol, and finally with a small quantity of ether. By means of a vacuum pump air is now drawn through the flask, or the air may be pumped through it by means of a foot bellows until it is dry.

**Fire.** Many of the common organic solvents, such as alcohol and ether, are very inflammable, and great care should be exercised in using them. When evaporating solutions of substances dissolved in these solvents, the evaporation should always be done on a previously heated water bath, and care should be taken that no lighted burners are near by. In case a beaker containing an inflammable solvent takes fire, the flame may be extinguished by simply placing a piece of sheet asbestos on top of the beaker. Should the vapors

continue to burn at the lip of the beaker, place a moist towel over this opening and the flame will be wholly extinguished. The flame may be extinguished also by placing a moist towel over the top of the beaker.

**Manipulation.** Many experiments require a somewhat elaborate apparatus, and it is usually necessary to have the various parts of the apparatus adjusted properly in order to obtain a satisfactory result. In performing an experiment it is best, first, to adjust the apparatus, and then ask an instructor to inspect it before proceeding further. When the apparatus has been properly set up, the student may proceed to weigh, or measure out, the materials which are to be used and continue according to the laboratory directions. In the case of certain experiments it is best to prepare the materials and allow them to stand a few days before using. In such cases the laboratory notes will give the necessary information as to the procedure. In using apparatus which has glass stopcocks, such as separating funnels, the stopcock should always be greased with burette grease; otherwise it is apt to "stick," and to break when being used. A good burette grease may be prepared by warming a mixture of three parts of vaseline and two parts of paraffin. To this is added one part of black rubber tubing that has been cut into small pieces. The mixture is heated until the rubber is dissolved, and is then poured into a bottle. Small bottles of burette grease may be obtained from the stock room or the side shelves.

**Accidents.** When a piece of glass tubing, or a thermometer, is to be passed through a stopper, always hold the tubing or thermometer near the end which first enters the stopper. If it is held at the farther end, it may break and the hand may receive a disagreeable cut. Cuts should be washed with running water, after which they should be treated with an antiseptic solution, such as dilute potassium permanganate or boric acid, and bandaged. Burns caused by acids should be washed with running water, after which they should be treated immediately with a concentrated solution of sodium bicarbonate.

**Solutions.** The concentration of solutions is frequently expressed as (1:10), which means, in the case of salt solutions, one gram of the salt dissolved in 10 cubic centimeters of water; in the case of acid solutions, such as sulfuric acid, a concentration of (1:10) means 1 cubic centimeter of the concentrated acid diluted with water to a volume of 10 cubic centimeters. A dilute solution of ammonia (1:10) is prepared by diluting 1 cubic centimeter of concentrated ammonium hydroxide with water to a volume of 10 cubic centimeters.



**Method of work.** Students should work independently as much as possible. All experiments which do not require a considerable length of time, or very much manipulation of apparatus, should be performed by each student. The more experience a student acquires in working with the chemicals and in manipulating the apparatus, the easier it is for him to understand the subject. Before performing an experiment the student should read carefully the preceding lecture notes and the experimental directions. Each student should have a notebook and write in it the equations of each experiment performed, and answer all questions asked in the lecture notes and those which are given at the end of the chapters.

In preparing compounds the product obtained should be purified, after which it should be weighed to ascertain the exact yield. The exact percentage of theoretical and actual yield obtained also should be calculated. In the case of test tube experiments, or preparations which are gases, it is not necessary to calculate the yield. The laboratory notes give directions for purifying compounds and state how to make the calculations. Laboratory notebooks should be written in the laboratory while the experiments are being performed or immediately after they are finished.

## II. APPROXIMATE QUANTITY OF MATERIALS REQUIRED FOR ONE STUDENT

MATERIALS	QUANTITY IN GRAMS
Acetamide . . . . .	40
Acetic anhydride . . . . .	30
Acetone . . . . .	20
Acetyl chloride . . . . .	1
Acid, acetic (glacial) . . . . .	300
Acid, acetic (monochlor) . . . . .	35
Acid, benzoic . . . . .	2
Acid, ethylene succinic . . . . .	1
Acid, formic . . . . .	20
Acid, hydrochloric . . . . .	700
Acid, lactic . . . . .	12
Acid, nitric . . . . .	200
Acid, oxalic . . . . .	107
Acid, phthalic (ortho) . . . . .	10
Acid, salicylic . . . . .	1

MATERIALS	QUANTITY. IN GRAMS
Acid, sulfuric . . . . .	1100
Acid, tannic . . . . .	9.5
Acid, tartaric (dextro) . . . . .	5
Acid, uric . . . . .	1
Aluminium sulfate . . . . .	5.
Ammonium chloride . . . . .	20
Ammonium hydroxide . . . . .	200
Ammonium sulfate . . . . .	24
Amylene . . . . .	5
Aniline . . . . .	60
Anthracene . . . . .	10
Antimony trioxide . . . . .	6
Azoxy benzene . . . . .	5
Benzaldehyde . . . . .	60
Benzene . . . . .	50
Benzoyl chloride . . . . .	5
Benzyl chloride . . . . .	30
Bromine . . . . .	150
Calcium carbide . . . . .	15
Calcium carbonate . . . . .	200
Calcium chloride . . . . .	78
Calcium oxide . . . . .	100
Carbon tetrachloride . . . . .	10
Catechol . . . . .	1
Chloroform . . . . .	10
Chromium trioxide . . . . .	20
Coal . . . . .	30
Coconut oil . . . . .	30
Congo red . . . . .	0.5
Copper carbonate . . . . .	2
Copper oxide . . . . .	12
Copper sulfate . . . . .	21
Copper turnings . . . . .	5
Dimethyl aniline . . . . .	20
Dimethyl sulfate . . . . .	25
Dinitro benzene (meta) . . . . .	12
Ether . . . . .	1500
Ethyl acetate . . . . .	20

MATERIALS	QUANTITY IN GRAMS
Ethyl alcohol (absolute) . . . . .	400
Ethyl alcohol (95 per cent) . . . . .	500
Ethyl bromide . . . . .	10
Ferric chloride . . . . .	7
Ferrous chloride . . . . .	5
Glucose . . . . .	1
Glycerol . . . . .	32
Iodine . . . . .	11
Iron filings . . . . .	16
Lead acetate . . . . .	19
Lead dioxide . . . . .	4
Lead oxide . . . . .	7
Manganese dioxide . . . . .	21
Mercuric chloride . . . . .	2
Mercuric cyanide . . . . .	2
Methyl benzoate . . . . .	1
Methyl salicylate . . . . .	12
Naphthalene . . . . .	20
Naphthol (alpha) . . . . .	1
Nitro benzene . . . . .	60
Petroleum ether . . . . .	30
Phenol . . . . .	55
Phosphorus pentoxide . . . . .	30
Phosphorus trichloride . . . . .	12
Potassium bromide . . . . .	45
Potassium carbonate . . . . .	55
Potassium chromate . . . . .	4
Potassium cyanate . . . . .	12
Potassium cyanide . . . . .	30
Potassium dichromate . . . . .	135
Potassium ferricyanide . . . . .	5
Potassium ferrocyanide . . . . .	5
Potassium hydroxide . . . . .	105
Potassium hydrogen tartrate . . . . .	7
Potassium iodide . . . . .	2
Potassium nitrate . . . . .	40
Potassium permanganate . . . . .	10
Potassium thiocyanate . . . . .	5

MATERIALS	QUANTITY IN GRAMS
Quinol . . . . .	0.5
Resorcinol . . . . .	0.5
Silver nitrate . . . . .	5
Soda lime . . . . .	50
Sodium acetate (fused) . . . . .	75
Sodium acetate (crystallized) . . . . .	6
Sodium carbonate (powder) . . . . .	115
Sodium chloride . . . . .	100
Sodium formate . . . . .	1
Sodium hydrogen carbonate . . . . .	25
Sodium hydrogen sulfite . . . . .	45
Sodium hydroxide . . . . .	235
Sodium (metallic) . . . . .	0.5
Sodium nitrite . . . . .	40
Sodium potassium tartrate . . . . .	12
Sodium sulfate . . . . .	10
Starch . . . . .	1
Sucrose . . . . .	32
Tartar emetic . . . . .	0.3
Tin . . . . .	70
Toluene . . . . .	20
Toluidine (para) . . . . .	25
Urea . . . . .	10
Zinc chloride (anhydrous) . . . . .	32
Oil (high boiling point for oil bath) . . . . .	300 cc.

### III. APPARATUS REQUIRED FOR ONE STUDENT

1 adapter	4 flasks (distilling, 50, 100, 200, 500 cc.)
2 asbestos wire gauzes	3 flasks (Erlenmeyer, 50, 100, 200 cc.)
2 Bunsen burners	1 flask (filtering, 500 cc.)
2 calcium chloride tubes	4 flasks (Florence, 50, 100, 300, 500 cc.)
4 clamps	2 funnels (65 mm.)
4 clamp holders	1 funnel (dropping, 50 cc.)
1 condenser	1 funnel (separating, 250 cc.)
1 cork borer, set of 3	1 funnel stand
1 crucible tongs	4 ft. glass tubing (inside diameter 4 mm.)
1 cylinder (100 cc. graduated)	3 iron rings
3 evaporating dishes (10, 12, 20 cm.)	2 iron stands
1 file (round)	1 mortar and pestle
1 file (triangular)	1 nest of beakers (50 to 600 cc.)
1 fishtail burner	
1 flask (1 liter round bottom)	

- 1 oil bath  
 1 package filter paper (11 cm. diameter)  
 1 pinch clamp  
 1 ft. rubber tubing (black, diameter 3 mm.)  
 5 ft. rubber tubing (Bunsen)  
 1 screw clamp  
 1 spatula (porcelain)  
 12 test tubes (160 X 15 mm.)
- 1 test tube brush  
 1 test tube (hard glass)  
 1 test tube holder  
 1 test tube rack  
 1 thermometer (360°)  
 1 towel  
 2 tripods  
 1 water bath  
 2 watch glasses (3" diameter)

## IV. ATOMIC WEIGHTS OF THE COMMON ELEMENTS

ELEMENT	SYMBOL	ATOMIC WEIGHT	ELEMENT	SYMBOL	ATOMIC WEIGHT
Aluminium . . .	Al	27.1	Magnesium . . .	Mg	24.32
Antimony . . .	Sb	120.2	Manganese . . .	Mn	54.03
Arsenic . . . .	As	74.96	Mercury . . . .	Hg	200.6
Barium . . . .	Ba	137.37	Molybdenum . .	Mo	96.0
Bismuth . . . .	Bi	208.0	Nickel . . . .	Ni	58.68
Boron . . . .	B	11.0	Nitrogen . . . .	N	14.01
Bromine . . . .	Br	79.92	Oxygen . . . .	O	16.00
Cadmium . . . .	Cd	112.40	Phosphorus . . .	P	31.04
Calcium . . . .	Ca	40.07	Platinum . . .	Pt	195.2
Carbon . . . .	C	12.00	Potassium . . .	K	39.10
Chlorine . . . .	Cl	35.46	Selenium . . . .	Se	79.2
Chromium . . . .	Cr	52.0	Silicon . . . .	Si	28.3
Cobalt . . . .	Co	58.97	Silver . . . .	Ag	107.88
Copper . . . .	Cu	63.57	Sodium . . . .	Na	23.00
Fluorine . . . .	F	19.0	Strontium . . .	Sr	87.63
Gold . . . .	Au	197.2	Sulfur . . . .	S	32.06
Hydrogen . . .	H	1.008	Tellurium . . .	Te	127.5
Iodine . . . .	I	126.92	Tin . . . .	Sn	118.7
Iron . . . .	Fe	55.84	Titanium . . .	Ti	48.1
Lead . . . .	Pb	207.2	Tungsten . . . .	W	184.0
Lithium . . . .	Li	6.94	Zinc . . . .	Zn	65.37

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